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VIII. *On the Determination of Chemical Affinity in terms of Electromotive Force.*—Part VIII. *By C. R. ALDER WRIGHT, D.Sc. (Lond.), F.R.S., Lecturer on Chemistry and Physics, and C. THOMPSON, Demonstrator of Chemistry, in St. Mary's Hospital Medical School\*.*

[Plate V.]

*On the Electromotive Force set up during Interdiffusion.*

147. It is well known that the E.M.F.'s of cells like those of Daniell and of Grove vary with the degree of concentration of the solutions used therein, and many measurements of the amounts of such variations have been from time to time published by different experimenters, *e.g.* by Regnault (*Ann. de Chim. et de Phys.* [3] xliv. p. 453), Svanberg (*Pogg. Annalen*, lxxiii. p. 290 [1848]); and more recently by Streintz (Carl. *Rep.* xv. p. 6 [1879]), Baumgartner (*ibid.* xv. p. 105 [1879]), and Fromme (*Annalen der Physik*, viii. p. 326 [1879]). From various causes, the nature of which will be apparent later on, the figures obtained by different observers do not exhibit such a degree of concordance as to lead to the establishment of any fundamental principle coordinating the variation in E.M.F. with the degree of dilution of the solutions used, excepting this

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general rule, that when the strength of the copper sulphate in a Daniell cell or of the nitric acid in a Grove's cell is decreased, a fall in the E.M.F. results ; and that when the strength of the solution surrounding the zinc is decreased, a rise in E.M.F. ensues, provided the solution is one of zinc sulphate : with other salts, and with dilute sulphuric acid, some observations indicate rise, others fall, in E.M.F. with decrease of strength.

It has been shown by Moser (*Annalen der Physik*, iii. p. 216 [1878]) that when two solutions of the same metallic salt, but of unequal strengths, are allowed to communicate so as to mix by interdiffusion, a current is set up passing from the weaker to the stronger solution through the fluid when electrodes are employed of the metal contained in the salt used (*e.g.* zinc for solutions of zinc sulphate, copper for solutions of copper sulphate, and so on) ; whilst the experiments described in Part V. (§ 110) indicate that the variations in E.M.F. of a Daniell cell containing zinc-sulphate solution round the zinc, according as the zinc-sulphate or the copper-sulphate solution varies in strength, are approximately equal numerically to the values obtained by Moser as the E.M.F.'s set up by the interdiffusion of solutions of zinc sulphate or of copper sulphate respectively, with the same limits of strength of solution.

It seemed of interest to pursue this point further, so as to decide by accurate measurements how far this approximation is merely an accidental coincidence : accordingly a large number of experiments have been made, mostly described in the following pages.

At first the observations were made by means of the quadrant electrometer, no permanent current passing ; but it was found that the experimental and observational errors were such that unless a very large number of duplicate cells were prepared and very many observations made with each, involving an immense expenditure of labour and time, trustworthy averages could not be obtained. The electrometer-readings (deflections on both sides of zero) could, at best, be read to no nearer than  $\pm 0.0025$  volt ; so that averages for single-cell values with a probable error of not more than  $\pm 0.01$  volt (one millivolt) entailed a large number of readings for each cell ; and as the values for different cells thus obtained exhi-

bited a range of several millivolts, numerous duplicate cells had to be set up to obtain a final mean with a probable error of less than  $\pm 1$  millivolt as the E.M.F. of each kind of cell; whilst, finally, the differences between the mean E.M.F.'s thus obtained exhibited, when plotted, deviations from a regular mean curve approaching to  $\pm 1$  millivolt, even with the utmost care in making observations and the bestowal of much time in so doing. Accordingly, the method of observation was changed, a delicate galvanometer being substituted for the electrometer; the instrumental errors being smaller and the sensitiveness greater\*, the same degree of accuracy (*i. e.* the same limits of probable error) were found to be attainable with a notably smaller number of observations, provided that certain precautions were observed, detailed more fully later on (§§ 149, 150). It was soon found, however, that the observance of these precautions sufficed to permit of the method of opposition being used so as to obtain directly the difference in E.M.F. between two cells alike in all respects, save that the zinc (or copper) sulphate solution used in one was stronger than that in the other. The values thus obtained led to sensibly the same mean curves as those obtained with a far greater amount of labour by means of the electrometer, and, notwithstanding the diminution in the number of observations, the range of probable error was sensibly diminished.

\* The galvanometer (by Elliott) was capable of being adjusted so as to give a total deflection, reading on both sides of zero with a reversing-key, of upwards of 200 scale-divisions when the current from a Daniell cell was passed through a resistance of 100,000 ohms, using the  $\frac{1}{1000}$  shunt; so that one scale-division =  $\frac{1.114}{1000 \times 100,000 \times 200}$  ampere =  $0.00056$  micro-ampere.

It being convenient to have some term representing the millionth of a millionth ( $0.0000000001 = 10^{-12}$ ), it is proposed to use the prefix "elasso" for this purpose (from  $\epsilon\lambda\alpha\sigma\sigma\omega\nu$ ), just as "micro" represents  $10^{-6}$ , and "mega" represents  $10^6$ : the value of 1 scale-division as above then becomes 56 elasso-amperes. The fraction  $0.00000001 = 10^{-9}$  may be conveniently represented by the double prefix "milli-micro," using each half in its ordinary sense; so that a centimetre = 1 milli-micro earth-quadrant. In the same kind of way 1,000,000,000 ohms may be termed a kilomegohm; and a million of million ergs may be spoken of as a meizerg ( $\mu\epsilon\zeta\omega\nu$ ). This nomenclature seems to be practically more convenient than such terms as twelfth-ampere, ohm-nine, erg-twelve, &c.

One of the essential precautions being the avoidance of diminution in E.M.F., in consequence of so-called "polarization," by using currents of only minute density, it at once suggested itself that under these conditions in all probability the difference of potential set up between (for example) two plates of zinc immersed in zinc-sulphate solutions of different strengths allowed to intermix by interdiffusion (or what may be conveniently called a *diffusion-cell*) would vary little, if at all, from that set up between the same two plates immersed in the same solutions respectively when these solutions are not directly connected so as to interdiffuse, but are severally connected (by any of the means used in two-fluid cells) with solutions of copper sulphate of identical strengths, in which are immersed copper plates of the same surface-character connected together by a wire : *i.e.*, that subsisting between the terminal plates of two opposed Daniell cells containing the same copper-sulphate solution, but zinc solutions differing from each other in strength and respectively identical with those used in the diffusion-cell, when the copper plates are united together and the zinc plates are the terminals. On trying the experiment this was found to be the case, *sensibly identical mean curves being obtained for given variations in solution-strength and for given kinds of plate-surfaces, whether the method of opposition was used, or that of diffusion-cells.*

148. Whichever method of observation was employed, the following general laws were always verified with a high degree of exactitude whenever sufficient observations were taken to get average results with only a small probable error. All the observations were carried out in every instance at a temperature within a very few degrees of 18° C., almost invariably between 15° and 20°.

(1) In any two-fluid cell containing solutions of two metallic salts and plates of the respective metals contained therein, an *increase in strength of the solution surrounding the plate acquiring the higher potential, in virtue of the normal action of the cell* (*i.e.* the plate functioning as the copper plate of a Daniell cell), *causes an increment in the potential-difference set up between that plate and the other.* The opposite effect is always produced by an increase in the strength of the solution surrounding the other plate. The increment and decrement

thus producible are, in certain cases, very considerable: with a Daniell cell a difference of nearly 6 centivolts (or upwards of 5 per cent. of the total E.M.F.) is producible, according as strong copper-sulphate and weak zinc-sulphate solutions are taken, or *vice versa*; with cells containing zinc and cadmium chlorides analogous differences up to even 30 centivolts are thus producible.

(2) A "law of summation" holds, expressible thus:—*The effect of the sum of a series of changes in the strengths of the solutions in a two-fluid cell is equal to the algebraic sum of the effects of each change severally.* Thus, by increasing the strength of the copper-sulphate solution in a Daniell cell (from, say,  $\cdot 25 \text{ CuSO}_4 100 \text{ H}_2\text{O}$  \* to  $2\cdot 0 \text{ CuSO}_4 100 \text{ H}_2\text{O}$ ), a given increment in E.M.F. ensues, =  $a$ : by similarly varying the zinc-sulphate solution (from, say,  $\cdot 25 \text{ ZnSO}_4 100 \text{ H}_2\text{O}$  to  $5\cdot 0 \text{ ZnSO}_4 100 \text{ H}_2\text{O}$ ), a decrement ensues, =  $b$ . Then the difference in E.M.F. between two cells, one containing  $\cdot 25 \text{ CuSO}_4 100 \text{ H}_2\text{O}$  and  $\cdot 25 \text{ ZnSO}_4 100 \text{ H}_2\text{O}$ , and the other containing  $2\cdot 0 \text{ CuSO}_4 100 \text{ H}_2\text{O}$ , and  $5\cdot 0 \text{ ZnSO}_4 100 \text{ H}_2\text{O}$ , is the sum of these amounts, *i. e.* is  $a - b$ ; so that if  $e$  is the E.M.F. of the first and  $E$  that of the second,  $E = e + a - b$ .

Similarly, if three cells be compared, alike in all respects save that the copper-sulphate solutions have (for example) the strengths  $\cdot 25 \text{ CuSO}_4$ ,  $1\cdot 0 \text{ CuSO}_4$ , and  $2\cdot 0 \text{ CuSO}_4$  (per  $100 \text{ H}_2\text{O}$  in each case), the excess of E.M.F. of the second over the first being experimentally found =  $c$ , and that of the third over the second being similarly found =  $d$ , then  $a = c + d$ .

(3) The values of  $a$ ,  $b$ ,  $c$ ,  $d$ , ..... are independent, not only of the actual strength of the solution which does not vary in any two cells compared, but also of the nature of that solution and of the metal immersed in it.

For example, in zinc-copper-sulphate cells with amalgamated zinc and electro-copper plates, the effect of a given alteration in the strength of the zinc-sulphate solution is sensibly the same whether the copper-sulphate solution be strong or weak; and, further, is precisely the same in zinc-cadmium-sulphate, or in zinc-silver-sulphate cells set up with amalgam-

\* Instead of expressing molecular strengths in the form  $\text{MSO}_4 n\text{H}_2\text{O}$ , and so on, it is more convenient for certain purposes to express them in the form  $m\text{MSO}_4 100\text{H}_2\text{O}$ , and so on.

mated zinc plates. Similarly, the numerical value of the effect of a given alteration in the strength of the copper-sulphate solution is the same whether the zinc-sulphate solution be strong or weak ; and, further, is still the same in copper-cadmium-sulphate or copper-silver-sulphate cells set up with electro-copper plates \*.

(4) The values of  $a, b, c, d, \dots$  vary perceptibly with the nature of the plate-surface of the metal immersed in the varying solution ; i. e. they are not constant for a given difference in strength if the plate-surface vary. In the case of the metals copper, zinc, and cadmium the highest values are observed, *ceteris paribus*, with plates superficially amalgamated, the amalgam being fluid ; plates freshly electro-coated give lower values, and bright polished plates of fused metal lower values still.

(5) With the majority of kinds of plate-surface examined, the values of  $a$  and  $b$  in the expression

$$E = e + a - b$$

are such that  $a$  and  $b$  are unequal in magnitude for equal amounts of variation in the strength of the two solutions in a two-fluid cell. Sometimes  $a$  increases more rapidly than  $b$  in numerical value as the solution-strength increases ; in which case the E.M.F. of the combination rises with the strength of the solutions when both are always of equal molecular strength : such a case is presented by a zinc-copper-sulphate cell with electro-zinc and amalgamated copper plates (§ 154). Sometimes the opposite is the case, e. g. a zinc-cadmium-chloride cell with amalgamated zinc and electro-cadmium plates (§ 156). Zinc-copper-sulphate cells set up with amalgamated zinc and electro-copper plates show the peculiarity that  $a$  and  $b$  are nearly equal numerically for all solution-strengths ; so that the E.M.F. of such a Daniell cell is practically invariable no matter what the strength of the solutions of zinc and copper sulphate used, provided that these are of the same molecular strength.

(6) On contrasting the values of  $a, b, c, d, \dots$  with the

\* In copper-silver-sulphate cells the effect of a given increment in the strength of copper-sulphate solution is, of course, to diminish the E.M.F. of the cell, and not to increase it as in zinc-copper-sulphate cells.

E.M.F.'s corresponding to the amounts of heat developed on intermixture of gramme equivalents of the two strengths of the varying solution compared together, *the former are usually found to exceed the latter*, sometimes by a very considerable amount.

149. In carrying out observations by means of either the method of opposition or that of diffusion-cells, it is obvious that the current observed produced through a given total resistance only represents the E.M.F. due to difference of solution-strength, provided that the two zinc plates and the two copper plates are identical in surface-characters, and provided also that the current-density is small enough to reduce polarization to negligible amounts. In practice it is impossible to ensure equality of surface with any pair of plates, even though prepared with the greatest care in precisely the same way from the same mass ; and the result is that when two plates, apparently identical, are immersed in the same solution, one is sufficiently electropositive with reference to the other to cause a distinctly measurable current to flow through even a large external resistance. In order to form some estimate as to the probable magnitude of this source of error, a large number of observations were made with pairs of zinc plates immersed in zinc-sulphate solutions of varying strengths, and pairs of copper plates immersed in copper-sulphate solutions. The following results in millivolts were obtained with upwards of 120 pairs of plates, readings being taken every few minutes for about half an hour after the first immersion, and being then averaged. As a rule the currents observed increased somewhat as time elapsed, so that the first readings were usually the minima. The galvanometer-readings were translated into volts by means of the formula

$$e = \frac{m}{n} \cdot \frac{R_2}{R_1} \cdot \frac{D}{1000} = mR_2 \cdot C,$$

where  $m$  = the galvanometer-reading to be translated (no shunt being used).

$n$  = the galvanometer-reading when a Daniell cell of E.M.F.  $D$  is used to send a current through a total resistance  $R_1$  ohms, employing  $\frac{1}{1000}$  shunt.

$R_2$  = total resistance in circuit when the reading  $m$  is taken.

$C$  = current representing 1 scale-division =  $\frac{D}{1000nR_1}$  amperes.

If the potential differences are expressed in millivolts, then

$$e = \frac{m}{n} \cdot \frac{R_2}{R_1} \cdot D.$$

Bright Zinc Plates.			
Molecular strength of solution, per 100 H <sub>2</sub> O.	Near 5 MSO <sub>4</sub> .	MSO <sub>4</sub> to 2 MSO <sub>4</sub> .	·25 MSO <sub>4</sub> to ·5 MSO <sub>4</sub> .
Maximum .....	1·49	3·65	12·5
Minimum .....	·07	·32	·32
Average .....	·69	2·13	5·45
Amalgamated Zinc Plates.			
Maximum .....	·11	·15	1·55
Minimum .....	·01	·02	·01
Average .....	·07	·09	·69
Bright Copper Plates.			
Maximum .....	.....	3·15	2·6
Minimum .....	.....	·65	·48
Average .....	.....	1·95	1·53
Recently coated Electro-copper Plates.			
Maximum .....	.....	·66	·22
Minimum .....	.....	·03	·03
Average .....	.....	·21	·14
Amalgamated Copper Plates.			
Maximum .....	.....	·54	1·4
Minimum .....	.....	·08	·27
Average .....	.....	·28	1·0

As a general rule the weaker the solution the greater is the average difference of potential set up between two plates, as alike as practicable, immersed in the same fluid: *caeteris paribus*, bright plates show much wider limits of variation than amalgamated or electro plates.

It being impossible to ensure equality of surface-conditions

by simply taking pains to make plates as alike as practicable, an approximation to the value that would have been obtained, had the plates been equal in surface-conditions, was arrived at in each experiment by the simple device of exchanging the plates after one series of readings had been taken, and taking another series of readings, averaging the two mean values thus obtained. In many cases the plates were exchanged twice more, and the general mean of all four sets of readings taken. To prevent alteration of solution-strength, the plates exchanged were always rinsed with the solution into which they were about to be dipped before immersion therein. Operating in this way, the difference between the values obtained before and after exchanging represents *double* the sum of the potential difference that would be set up between the plates when opposed to one another in the same solutions respectively. It is noteworthy that the figures thus got by exchanging plates are of the same order of magnitude as those resulting from the opposition of two plates of the same kind. Thus in the above-described experiments the maximum variation observed with amalgamated zinc plates is 1.55 millivolt, and that with electro-copper plates .66 millivolt, giving a sum of 2.21; whilst the corresponding average values give a sum of less than .5 millivolt. With two opposed Daniells set up with amalgamated zinc and electro-copper plates, the halves of the differences observed on exchanging plates averaged less than .5 millivolt, sometimes, however, amounting to 1.0, and occasionally, but only rarely, to 2.0 millivolts; and similarly in other cases.

150. In order to eliminate errors arising from depreciation of E.M.F. through non-adjuvancy, arising from the current-density being greater than the limiting-density below which such effects are inappreciable ("polarization"), several series of observations were made in order to find out what the limiting-densities are for different kinds of plates and fluids, such that the depreciation in E.M.F. shall not exceed a definite small quantity, say .1 to .2 millivolt. The experiments already published made with single Daniell and other analogous cells (§§ 103-105, Part V.) show that with current-densities of from 10 to 20 microampères per square centimetre of plate-surface (both plates being equal in area, and

one only being reckoned), diminutions in E.M.F. of from 1 to 6 millivolts may be brought about, quantities in many cases far exceeding the potential-differences due to varying solution-strength to be measured. Manifestly, therefore, only very minute currents can be employed when two Daniell or other analogous cells are opposed, and consequently the effect of "polarization" about doubled. Similarly the experiments described in Part IV. (§ 93) indicate that when a current passes between two zinc plates in zinc-sulphate solution, or between two copper plates in copper-sulphate solution, a "counter electromotive force" of a considerable number of millivolts, and even some centivolts, may be set up with current-densities of but a few microamperes per square centimetre; so that in a "diffusion-cell" serious diminutions in the potential-difference actually set up may be brought about by very small current-densities.

In order to determine these limiting current-densities, experiments were made in the following way. The diffusion-cell, or pair of opposed Daniell or other cells to be examined, was set up, as was also a normal Daniell cell for comparison, and the currents from each alternately sent through a large external resistance (using appropriate shunts), series of readings being taken in each case. The resistance was now altered, and two fresh series of readings taken; after which it was again altered, and two more series taken, and so on: usually the whole set of series of readings was repeated in reverse order. The average scale-readings for a series of given total resistances in circuit were thus known both for the Daniell cell and the other one compared with it. With the former, the product of average scale-reading and total resistance was sensibly constant for current-densities that caused an appreciable falling-off in the product similarly obtained with diffusion-cells or with two opposed Daniell cells, &c., showing that whilst "polarization" did not occur to a measurable extent in the first case, it did in the second. The following illustration will make the point clear: two series of readings with varying resistances were made in reverse order with a normal Daniell cell, and with two opposed cells jointly giving an effective E.M.F. of a little more than one-hundredth of that of the Daniell cell; for the

former the  $\frac{1}{2000}$  shunt was used, and for the latter the  $\frac{1}{10}$  shunt.

### Single Daniell Cell.

Total resist- ance in circuit, in ohms.	Scale-readings.			Product of mean scale-reading into resistance.
	First series.	Reversed series.	Mean.	
200,050	63.7	63.9	63.8	$12.763 \times 10^6$
150,050	84.8	85.3	85.05	$12.762 \times 10^6$
100,050	127.5	127.6	127.55	$12.761 \times 10^6$

Here the product of scale-reading into resistance being constant within the limits of observational error, it is evident that the E.M.F. of the cell was constant within about  $\frac{1}{2000}$  part of its value, notwithstanding that the current rose from  $\frac{1.11}{200050}$  ampere (5.5 microamperes) to  $\frac{1.11}{100050}$  ampere (11.1 microamperes), representing a rise in density of from 2 to 4 microamperes per square centimetre, the plates exposing a surface of about 3 square centimetres each. Each scale-division here represented  $\frac{1.115}{1000 \times 12.762 \times 10^6}$  ampere, or 87.37 classoamperes.

### Two opposed Cells.

Total resist- ance, in ohms.	Scale-readings.			Current, in microamperes.	E.M.F. in milli- volts.	Fall in E.M.F.
	First series.	Reversed series.	Mean.			
200,820	69.3	70.1	69.7	.060897	12.23	—
150,820	92.1	93.25	92.67	.080965	12.21	.02
100,820	137.0	138.0	137.5	.120134	12.11	.11

Hence with an increase of current from .06 to .08 microampere, representing an increase in density from .02 to .027, the fall in E.M.F. was barely measurable, being only .02 millivolt; but when the current rose to .12 microampere, giving a density of .04, the fall in E.M.F. was distinct, being upwards of .1 millivolt.

151. In the same kind of way various other observations were made, and indicated on the whole that the effect of polarization in cells set up with amalgamated-zinc and electro-

copper plates is not greater than about  $\cdot 2$  millivolt, as long as the current-density does not exceed about  $\cdot 05$  microampere per square centimetre of plate-surface.

Limiting values not far from this were similarly obtained with other kinds of zinc- and copper-plate surfaces. Accordingly in the observations made with these kinds of cells for the purpose of estimating the variations in E.M.F. due to difference in solution-strength, the current-densities were never allowed to exceed this limit, and were usually a long way below it.

In precisely the same kind of way the limiting values for various kinds of diffusion-cells were arrived at. The following table represents some of the average results obtained, the E.M.F.'s being expressed in millivolts:—

Current-density, microamperes per square centimetre.	Two opposed Daniell cells.		Diffusion-cells.		
	Amalgamated zinc and electro-copper plates.	Zinc sulphate.		Copper sulphate.	
		Electro- zinc plates.	Amalgamated- zinc plates.	Electro- copper plates	
Not exceeding $\cdot 02$	Below $\cdot 02$	Below $\cdot 03$	Inappreciable	Inappreciable	
$\cdot 02$ to $\cdot 035$	$\cdot 0\cdot 1$	$\cdot 1$	Below $\cdot 1$	$\cdot 1$	$\cdot 1$
$\cdot 035$ " $\cdot 06$	$\cdot 1$ to $\cdot 3$	$\cdot 1$ to $\cdot 2$			
$\cdot 06$ " $\cdot 10$	$\cdot 3$ " $\cdot 5$	$\cdot 2$ " $\cdot 5$	$\cdot 1$ to $\cdot 2$	$\cdot 3$ " $\cdot 5$	$\cdot 1$ to $\cdot 3$
$\cdot 10$ " $\cdot 15$	$\cdot 5$ " $\cdot 8$	$\cdot 5$ " $1\cdot 0$			
$\cdot 15$ " $\cdot 2$	$\cdot 8$ " $1\cdot 2$		$\cdot 2$ " $\cdot 4$	$\cdot 5$ " $\cdot 8$	
$\cdot 2$ " $\cdot 5$			$\cdot 4$ " $1\cdot 0$	$\cdot 8$ " $2\cdot 0$	
$\cdot 5$ " $\cdot 8$			$1\cdot 0$ " $2\cdot 0$		

It is here noticeable that the amounts of depreciation for given increments in current-density observed with two opposed Daniell cells containing amalgamated-zinc and electro-copper plates are fairly close to the sums of those similarly observed for two diffusion-cells, one containing amalgamated-zinc and the other electro-copper plates. The chemical action in two opposed Daniell cells amounts to solution of copper in one cell and deposition thereof in the other, and ditto for zinc; or precisely the sum of the actions with two diffusion-cells.

The amount of depreciation for a given current-density increase varies notably with the metal and character of surface: thus amalgamated zinc gives less depreciation than electro-copper, and electro-copper less than electro-zinc. Variation in the strength of the solution used did not appear to influ-

ence the result to anything like so great an extent as variation in the nature of the plate-surfaces.

On the whole it was found, even in those cases where the maximum amount of depreciation was produced, that this depreciation did not exceed from '1 to '2 millivolt, until the current-density overpassed '02 to '03 microampere per square centimetre. In the four cases above cited the limiting current-densities, when the depreciation amounts to '2 millivolt, are:—

Two opposed Daniell cells, amalgamated-zinc and electro-copper plates .....	·05
Diffusion-cells, electro-zinc plates .....	·06
"      " amalgamated-zinc plates .....	·15
"      " electro-copper plates .....	·08

In carrying out the observations, therefore, care was taken\* that in no case should the current-density exceed the limiting value for the particular class of cell examined, current-densities of much less amount being in most cases employed; so that, finally, *the effect of "polarization" on the average values obtained is in no case to depreciate them by a quantity so great as ·2 millivolt, and is usually insufficient to depreciate by an amount approaching to ·1 millivolt.*

152. As a general rule, it was found that when the cell (or pair of opposed cells) to be examined was set up, comparatively little variation in the current flowing took place during 15 to 30 minutes; what alteration did occur being evidently due to alteration in condition of plate-surface (by superficial oxidation by dissolved air, or by molecular change, *i.e.* spontaneous change of state of aggregation, or by solution or deposition of external film as the current flowed producing electrolysis), and being only a fraction of the variation produced on exchanging plates. With bright zinc plates, however, the alteration during a few minutes after setting up was

\* Owing probably to the influence of "polarization," the values obtained by Fromme, *loc. cit. suprà*, do not exhibit very close concordance with one another, nor do the mean curves thence deducible agree sharply with those subsequently detailed. Moser's diffusion-cell figures, on the other hand, do not differ widely from those obtained by us.

often considerable and irregular in direction. The numbers given in the subsequent section are in all cases deduced from the average readings of the cells during the first 15 or 20 minutes after first setting up, or after exchanging plates, as the case might be; the mean of the two averages thus obtained (or of the four, if three exchanges were made after taking the first set of readings) being finally adopted as the mean value for the particular experiment.

As regards the experiments with the diffusion-cells, these were ordinarily constructed of two beakers united by an inverted Y-shaped tube, the ends of which were covered with bladder or other thin membrane, and filled with either of the two solutions used, one in one beaker, the other in the other: in short, they were precisely similar to the forms of Raoult cell used in the preceding portions of these researches. It was thought desirable to see if any influence could be traced as exerted by the membranes as such, and accordingly a number of gravity diffusion-cells were set up by pouring into a long U-tube the stronger of the two solutions used until rather more than half full, and then very cautiously running slowly into one limb the weaker solution, so as to have a well-marked line of demarcation between the two fluids. Two plates were then immersed in the two solutions and exchanged after taking readings, and so on. Both with zinc sulphate and copper sulphate no measurable differences could be detected between the average results obtained with these cells and with the Raoult form of cell, both sets of cells having respectively the same fluids and kinds of plates; clearly proving that the membranes as such exercised no measurable influence on the results.

As an illustration of the general character of the experiments made, the following observations with two opposed Daniell cells may be cited as an example, typical in all respects saving, first, that the values obtained before and after exchanging plates differ more than usual (for which reason this experiment is selected); and, secondly, that the galvanometer was regulated so as to be considerably less sensitive than was found desirable for other experiments, on account of the comparatively large potential-difference to be measured.

Plates used : amalgamated zinc and electro-copper.

Solutions used : per 100 H<sub>2</sub>O, 2·0 CuSO<sub>4</sub> throughout ; 5·584 ZnSO<sub>4</sub> in one cell and 1012 ZnSO<sub>4</sub> in the other.

Valuation of scale : a normal Daniell cell (set up with amalgamated zinc, electro-copper, and zinc- and copper-sulphate solutions of equal strength) gave 125·7 scale-degrees as mean reading when 200100 ohms were in circuit, the  $\frac{1}{100}$  shunt being used, whence 1 scale-division =  $\frac{1\cdot114}{100 \times 200100 \times 125\cdot7}$  ampere = 0·00443 microampere = 443 classoamperes.

Readings before exchanging plates.	After exchanging plates.
Average scale-reading (no shunt used)..... 484·25	467·0
Current passing, in micro-ampères*..... 2145	2069
Total resistance in circuit, in ohms .....	207400
E.M.F., in millivolts .....	44·5
Mean of the two results .....	43·7 millivolts.
Maximum departure between ditto .....	1·6 millivolt.
Difference from mean .....	$\pm$ 8 "

In the same kind of way other similar experiments gave means ranging from 41·6 to 44·4 millivolts, the final average being 43·3, with a probable error of  $\pm$  34 millivolt.

153. The following tables give, in millivolts, the results obtained with various kinds of metals, natures of plate-surfaces, and descriptions of saline solutions :—

### I. Variations of Potential due to Variations of Strength in Zinc-sulphate Solution.

#### 1. Amalgamated Zinc Plates.

##### A. Observations with the Electrometer.

Probable error of each value cited not exceeding  $\pm$  1·0 millivolt. The numbers represent the difference of potential set up when one solution is  $m$  ZnSO<sub>4</sub> 100 H<sub>2</sub>O, and the other  $n$  ZnSO<sub>4</sub> 100 H<sub>2</sub>O.

\* Representing a current-density of about 0·45 microampere per square centimetre.

Value of $m$ .	Value of $n$ .					
	4.2	3.0	2.1	1.1	.55	.167
5.1	4	12	16	23	28	37
4.2	.....	8	12	19	24	33
3.0	.....	.....	4	11	16	25
2.1	.....	.....	.....	7	12	21
1.1	.....	.....	.....	.....	5	14
.55	.....	.....	.....	.....	.....	9

B. With two opposed Daniell cells, the copper plates being united and the zinc plates the terminal ones, the following values were obtained. The probable error of each value cited is less than in the electrometer-experiments, being usually well within  $\pm .5$  millivolt, often no more than  $\pm .25$  millivolt.

Value of $m$ .	Value of $n$ .					
	3.995	3.005	2.158	1.016	.497	.1012
5.584	10.5	16.1	20.2	26.7	32.3	43.3
3.995	.....	5.6	9.7	16.2	21.8	32.8
3.005	.....	.....	4.1	10.6	16.2	27.2
2.158	.....	.....	.....	6.5	12.1	23.1
1.016	.....	.....	.....	.....	5.6	16.6
.497	.....	.....	.....	.....	.....	11.0

C. With Diffusion-cells the following values were obtained: probable error of each value less than  $\pm .5$  millivolt:—

Value of $m$ .	Value of $n$ .					
	3.95	3.10	2.00	.96	.50	.237
5.25	6.8	12.4	18.4	24.7	29.2	35.0
3.95	.....	5.6	11.6	17.9	22.4	28.2
3.10	.....	.....	6.0	12.3	16.8	22.6
2.00	.....	.....	.....	6.3	10.8	16.6
.96	.....	.....	.....	.....	4.5	10.3
.50	.....	.....	.....	.....	.....	5.8

On graphical representation all three sets of figures are found to accord fairly well when, by interpolation, the figures are all reduced to a common origin for the three curves, viz. when  $m=5.0$ . The following table gives the result thus reduced to common origin and the same abscissæ.

	Electrometer.	Two opposed cells.	Diffusion-cells.	Average.
5.584	.....	— 3.8		
5.25	.....	.....	— 1.3	
5.1	— 0.4	.....	.....	
5.0	0	0	0	0
4.0	4.8	6.7	5.2	5.6
3.0	11.6	12.3	11.6	11.8
2.0	16.3	17.3	17.1	16.9
1.0	23.5	23.1	23.1	23.2
.5	28.7	28.5	27.9	28.4
.237	34.9	35.7	33.7	34.8
.167	36.6	37.7	.....	37.2
.100	.....	39.5	.....	39.5

It is evident that, having regard to the impossibility of completely eliminating errors from difference of character of plate-surface, these numbers coincide sufficiently closely to show that whether no current at all circulates (electrometer), or a small current not too great to set up any notable "polarization," *sensibly the same numbers result whether the observations be made by carefully valuing separate cells and subtracting the values from one another; by opposing two cells and measuring the current due to the difference in their E.M.F.'s; or by means of diffusion-cells (representing the terminal liquids of two opposed cells of Raoult's form, when directly connected).* The same conclusions also follow from the observations detailed in § 154 made with copper-sulphate solution and electro-copper plates.

### 2. Electro-zinc Plates.

Observations made with Diffusion-cells only: probable error-in no case exceeding  $\pm .75$  millivolt.

	$n=3.005$	$n=1.016$	$n=.1012$
$m=5.584$	11.2	20.0	30.5
3.005	.....	8.8	19.3
1.016	.....	.....	10.5

### 3. Bright Zinc Plates.

Observations with Diffusion-cells only: very much less concordance between the results of these experiments than with other kinds of zinc plates, and much more alteration (and of more irregular character) on allowing cells to stand a few minutes.

Probable error about  $\pm 1.5$  millivolt.

	$n=3.005$	$n=1012$
$m=5.584$	10.0	29.6
$=3.005$	.....	19.6

The following table represents these three sets of values reduced by interpolation to a common origin ( $m=5.0$ ) and common abscissæ: the curves respectively marked 1, 2, and 3 in fig. 1, Plate V., indicate the three sets of reduced values thus obtained.

Difference of Potential set up between Solutions of  $5.0 \text{ ZnSO}_4 \text{ 100 H}_2\text{O}$  and  $n \text{ ZnSO}_4 \text{ 100 H}_2\text{O}$ .

	Amalgamated zinc (average above cited)	Electro- zinc.	Bright zinc.
$n=5.0$	0	0	0
$=3.0$	11.8	8.6	7.7
$=1.0$	23.2	17.5	15.8
$=0.1$	39.5	27.9	25.3

Evidently the values with amalgamated zinc are the highest, and those with bright zinc the lowest.

154. II. *Variations of Potential due to Variation in Strength of Copper-sulphate Solution.*

1. *Electro-copper Plates.*

A. Observations with the Electrometer. Probable error not exceeding  $\pm 1$  millivolt.

Values of $m$ .	Values of $n$ .		
	1.10	.55	.167
2.1	5	11	20.5
1.1	.....	6	13.5
.55	.....	.....	9.5

B. With two Opposed Cells. Probable error usually well within  $\pm 5$  millivolt, and often less than  $\pm 2.5$  millivolt.

	$n=.940$	$n=.461$	$n=.094$
$m=1.972$	5.6	10.3	22.4
$=.940$	.....	4.7	16.8
$=.461$	.....	.....	12.1

C. With Diffusion-cells. Probable error less than  $\pm .5$  millivolt.

	$n=99$	$n=.47$	$n=.227$
$m=1.88$	5.7	10.5	16.3
$=.99$	.....	4.8	10.6
$=.47$	.....	.....	4.7

On graphical representation after reduction, by interpolation, to common origin (when  $m=2.0$ ) and common abscissæ, these three sets of figures are found to coincide within reasonable error-limits, thus confirming the results arrived at above with amalgamated-zinc plates and zinc-sulphate solutions. Further, it is noticeable that these values are all close to those similarly obtained with zinc-sulphate solutions and amalgamated-zinc plates when similarly reduced.

Value of $m$ .	Electro-meter.	Two opposed cells.	Diffusion-cells.	Average.	Average with zinc sulphate and amalgamated-zinc plates.
2.1	-.5	.....	0	0	0
2.0	0	0	.....	.....	.....
1.972	.....	2	.....	.....	.....
1.88	.....	.....	-.8	.....	.....
1.0	5.6	5.5	6.4	5.8	6.3
.5	11.7	10.1	11.0	10.9	11.5
.227	18.5	18.2	17.1	17.9	18.2
.167	20.0	20.2	.....	20.1	20.3
.100	21.7	22.4	.....	22.0	22.6
.094	21.8	22.6	.....	.....	.....

It would hence result that the E.M.F. of a Daniell cell set up with zinc- and copper-sulphate solutions of the same molecular strength, and amalgamated-zinc and electro-copper plates, cannot exhibit any very marked variation, whatever the actual strength of the solutions, inasmuch as whatever effect on the E.M.F. is produced by a given variation in the strength of the zinc-sulphate solution must be very nearly counterbalanced by the equal and opposite effect of the same variation in the strength of the copper-sulphate solution. If, however, electro-zinc or bright zinc plates be used, the E.M.F. must rise with the strength of the solutions, the copper-sulphate variation effect overpowering the zinc-sulphate variation effect. In other words, if  $e$  be the E.M.F. of the cell for a

given low strength of solution, and  $E$  that for a greater strength, then  $E = e + a - b$  (§ 148): with amalgamated zinc and electro-copper plates,  $a$  nearly  $= b$ ; but with electro or bright zinc,  $a < b$ .

The following experiments show that the value of  $a$ , *cæteris paribus*, is greater with amalgamated, but less with bright, than with electro copper; so that with cells set up with amalgamated zinc plates, the value of the E.M.F. rises with the strength of the solutions when amalgamated copper plates are opposed, and falls when bright copper plates are used instead.

### 2. *Amalgamated Copper Plates.*

Observations with Diffusion-cells. Probable error not exceeding  $\pm .75$  millivolt.

	$n = .940$	$n = .461$	$n = .094$
$m = 1.972$	6.0	12.0	27.5
.940	.....	6.0	21.5
.461	.....	.....	15.5

### 3. *Bright Copper Plates partially but not completely Electro-coated.*

Observations with Diffusion-cells. Probable error not exceeding  $\pm .75$  millivolt.

	$n = .940$	$n = .461$	$n = .094$
$m = 1.972$	4.1	9.3	19.7
.940	.....	5.2	15.6
.461	.....	....	10.4

### 4. *Bright Copper Plates.*

Observations with Diffusion-cells. Probable error not exceeding  $\pm 1.0$  millivolt.

	$n = .461$	$n = .094$
$m = 1.972$	6.9	16.8
.461	.....	9.9

The following table represents these four sets of values reduced, by interpolation, to a common origin ( $m = 2.0$ ) and common abscissæ: the curves marked respectively 1, 2, 3, and 4, fig. 2, represent these sets of reduced values: curve 5 similarly represents the average values for amalgamated zinc and

zinc-sulphate solution similarly reduced; evidently nearly coinciding with curve 2 (electro-copper).

Difference of Potential set up between Solutions of  $2\cdot0\text{ CuSO}_4\text{ }100\text{ H}_2\text{O}$  and  $n\text{CuSO}_4\text{ }100\text{H}_2\text{O}$ .

	Amalgamated copper.	Electro-copper.	Bright copper only partially electro-coated.	Bright copper.
$n=2\cdot0$	0	0	0	0
$=1\cdot0$	5.9	5.8	4.0	3.5
$=\cdot5$	11.7	10.9	9.0	6.6
$=\cdot1$	27.2	22.0	19.6	16.8

155. A number of observations were similarly made with various cadmium-sulphate solutions, employing different kinds of cadmium plates: only diffusion-cells were used in this series of experiments. The following results were obtained as final average values, showing that amalgamated plates (wet with liquid amalgam) give higher, and bright plates lower values than electro-coated plates, just as with zinc and copper.

1. *Electro-cadmium Plates*.—Probable error of each value less than  $\pm\cdot5$  millivolt.

Value of $m$ .	Value of $n$ .					
	4.95	3.205	2.01	1.02	.46	.235
6.10	6.0	14.2	19.5	24.7	29.9	34.2
4.95	.....	8.2	13.5	18.7	23.9	28.2
3.205	.....	.....	5.3	10.5	15.7	20.0
2.01	.....	.....	.....	5.2	10.4	14.7
1.02	.....	.....	.....	.....	5.2	9.5
.46	.....	.....	.....	.....	.....	4.3

2. *Bright Cadmium Plates*.—Probable error less than  $\pm\cdot75$  millivolt.

Value of $m$ .	Value of $n$ .					
	4.95	3.205	2.01	1.02	.46.	.235.
6.10	4.9	13.7	18.5	23.0	27.4	30.5
4.95	.....	8.8	13.6	18.1	22.5	25.6
3.205	.....	.....	4.8	9.3	13.7	16.8
2.01	.....	.....	.....	4.5	8.9	12.0
1.02	.....	.....	.....	.....	4.4	7.5
.46	.....	.....	.....	.....	.....	3.1

3. *Amalgamated Cadmium.*—Surface wet with fluid amalgam. Probable error not exceeding  $\pm 0.75$  millivolt.

	$n=2.01.$	$n=1.02.$	$n=.235.$
$m=6.10.....$	20.6	26.3	35.9
$=2.01.....$	.....	5.7	15.3
$=1.02.....$	.....	.....	9.6

4. *Amalgamated Cadmium.*—Surface not fluid, but crystalline. Probable error not exceeding  $\pm 1.5$  millivolt.

	$n=2.01.$	$n=1.02.$	$n=.235.$
$m=6.10$	14.5	19.6	24.5
$=2.01$	.....	5.1	10.0
$=1.02$	.....	.....	4.9

The following tables are obtained from the above values by interpolation, as in the above observations with zinc and copper sulphates:—

Difference of Potential set up between Solutions of  $5.0\text{ CdSO}_4$   
 $100\text{ H}_2\text{O}$  and  $n\text{ CdSO}_4$   $100\text{ H}_2\text{O}$ .

	Amalgamated cadmium, fluid.	Electro- cadmium.	Bright cadmium.	Amalgamated cadmium, crystalline.
$n=5.0.....$	0	0	0	0
3.0.....	10.1	9.9	10.5	7.1
2.0.....	15.1	13.9	13.8	10.6
1.0.....	20.9	19.2	18.4	15.8
0.5.....	25.6	23.8	22.4	18.3
0.235.....	30.4	28.5	25.8	20.6

Difference of Potential set up between Solutions of  $2.0\text{ CdSO}_4$   
 $100\text{ H}_2\text{O}$  and  $n\text{ CdSO}_4$   $100\text{ H}_2\text{O}$ .

	Amalgamated cadmium, fluid.	Electro- cadmium.	Bright cadmium.	Amalgamated cadmium, crystalline.
$n=2.0.....$	0	0	0	0
$=1.0.....$	5.8	5.3	4.6	5.2
$=.5.....$	10.5	9.9	8.6	7.7
$=.235.....$	15.3	14.6	12.0	10.6

Curves 1 to 4 (figs. 3 and 4) represent these sets of values respectively: it is noticeable that the curve obtained with crystalline amalgam plate-surfaces underlies the others.

On contrasting the first of these tables with that similarly obtained with zinc sulphate (§ 153), and the second with that obtained with copper sulphate (§ 154), it is evident that with

certain kinds of plates the effect of an increase in strength of solutions (both being always of equal strength) is to produce an increase in E.M.F. in zinc-cadmium-sulphate cells or cadmium-copper-sulphate cells; and with other kinds of plates to produce a decrease: *i. e.* the values of  $a$  and  $b$  in the formula

$$E = e + a - b$$

are such that in certain cases  $a > b$  and in others  $b > a$ , precisely as is found with zinc-copper-sulphate cells. It is noticeable that even in the most extreme cases the difference between  $a$  and  $b$  is never very great, rarely exceeding a few millivolts.

156. For the sake of comparison with the amounts of heat developed on intermixture of strong and weak solutions, the following series of observations were made with solutions of zinc and cadmium chlorides, these salts being more especially selected because the calorimetric observations detailed later on (§ 160) showed that, whereas the heat of dilution of cadmium-sulphate solutions is greater than that of zinc-sulphate solutions, the opposite relationship holds with the solutions of the chlorides of these metals.

*Cadmium Chloride*.—Observations with diffusion-cells. Electro-cadmium plates: probable error of each value not exceeding  $\pm .5$  millivolt.

Value of $m$ .	Value of $n$ .					
	8·0.	4·45.	3·1.	2·1.	·67.	·25.
11·1	16·1	23·8	26·4	33·1	43·3	54·4
8·0	.....	7·7	10·3	17·0	27·2	38·3
4·45	.....	.....	2·6	9·3	19·5	30·6
3·1	.....	.....	.....	6·7	16·9	28·0
2·1	.....	.....	.....	.....	10·2	21·3
·67	.....	.....	.....	.....	.....	11·1

*Zinc Chloride.*—Observations with diffusion-cells. Amalgamated-zinc plates; probable error less than  $\pm 1.0$  millivolt.

On reducing these two sets of figures to the values for  $m=10$  as origin, and plotting the resulting numbers, the curves marked 1 and 2 respectively (Pl. V. fig. 5) are obtained: evidently the value of  $b$  in the expression  $E=e+a-b$  greatly exceeds that of  $a$  for all cases where equal molecular strengths of solutions are used in zinc-cadmium-chloride cells; *i. e.* the E.M.F. of a cell set up with zinc and cadmium chlorides, amalgamated zinc, and electro-cadmium decreases as the solution-strength increases, both solutions being equal in strength

A number of observations made with the galvanometer showed that this is the case, and that the value of the E.M.F. of any zinc-cadmium-chloride cell is given in volts by the equation

$$E = .330 + a - b,$$

where .330 is the E.M.F. of a cell containing amalgamated-zinc and electro-cadmium plates, and solutions of the chlorides of equal strength .25 MCl<sub>2</sub> 100 H<sub>2</sub>O; whilst  $a$  and  $b$  are the values deduced from the above tables for the difference of potential set up for solutions of this strength as compared with the particular strengths employed in the cell examined.

157. A noteworthy point in connexion with the value .330 volt for solutions .25 MCl<sub>2</sub> 100 H<sub>2</sub>O is the following. According to Julius Thomsen (*Journ. Prakt. Chemie*, xi. p. 402), the heats of formation of cadmium and zinc sulphates dissolved in 400 H<sub>2</sub>O (.25 MSO<sub>4</sub> 100 H<sub>2</sub>O) exhibit exactly the same difference as exists between those of cadmium and zinc chlorides dissolved in 200 H<sub>2</sub>O; thus:—

Zn, O, SO <sub>3</sub> , aq = 106090		Zn, Cl <sub>2</sub> , aq = 112840
Cd, O, SO <sub>3</sub> , aq = 89500		Cd, Cl <sub>2</sub> , aq = 96250
16590		16590

Consequently, as the heat of dilution of ZnCl<sub>2</sub> 200 H<sub>2</sub>O to ZnCl<sub>2</sub> 400 H<sub>2</sub>O exceeds that of CdCl<sub>2</sub> 200 H<sub>2</sub>O to CdCl<sub>2</sub> 400 H<sub>2</sub>O, and the excess is to be added to the above difference in the case of the chlorides, the heat evolved in the displacement of cadmium by zinc from CdCl<sub>2</sub> 400 H<sub>2</sub>O is slightly *greater* than that from CdSO<sub>4</sub> 400 H<sub>2</sub>O. The electromotive forces of zinc-cadmium-sulphate and zinc-cadmium-chloride cells for solutions of strengths MSO<sub>4</sub> 400 H<sub>2</sub>O, and MCl<sub>2</sub> 400 H<sub>2</sub>O (.25 MSO<sub>4</sub> and .25 MCl<sub>2</sub> per 100 H<sub>2</sub>O) do not ex-

hibit this relationship: on the contrary, the E.M.F. of the latter is materially *less* than that of the former; and, further, is distinctly less than that corresponding to the heat evolved in the net chemical change with which the E.M.F. of the former fairly coincides; thus:—

E.M.F. corresponding to 16590 grammes- degrees per gramme-molecule, or 8295 per gramme equivalent .....	} = ·365 volt.
Observed E.M.F. with zinc-cadmium-sul- phate cells set up with solutions of ·25 $\text{MSO}_4$ 100 $\text{H}_2\text{O}$ , amalgamated-zinc and electro-cadmium plates (§ 121, Part VI.) .....	= ·360 volt.
Observed E.M.F. with zinc-cadmium- chloride cells set up with solutions of ·25 $\text{MCl}_2$ 100 $\text{H}_2\text{O}$ , amalgamated-zinc and electro-cadmium plates.....	= ·330 ,

The difference between ·365 and ·330 volt, or ·035 volt, represents nearly 10 per cent. of the former value, and corresponds to upwards of 1500 gramme-degrees per gramme molecule, a quantity almost too large to be likely to be due solely to accumulation of experimental errors. This point will be further discussed in a future paper.

158. No material difference is made in the relationships between the E.M.F.'s observed (deduced from the assumption that the E.M.F. of Clark's cell = 1·457 volt) and those calculated from the heat-values (by using the factor 4410), when, instead of the numerical values 1·457 and 4410 for these quantities (hitherto purposely employed throughout for the sake of uniformity), the more exact values are used deduced from more recent observations on the true value of the B.A. unit of resistance, and especially those of Lord Rayleigh, which indicate that the true value is only  $·9868 \times 10^9$ . For the use of this corrected value reconciles the apparent discrepancy between Joule's various valuations of the mechanical equivalent of heat (§§ 33, 34, Part I.); and, further, causes all the different estimations of the value of  $J$  discussed in §§ 55 and 56 (Part III.) to agree fairly well together, and to become on reduction values close to the mean result of Joule's friction

experiments, viz.  $41.555$  megalergs (§ 34). Combining this value of  $J$  with the mean value of the "Faraday coefficient" (the quantity referred to in § 7, Part I., as indicated by  $\chi$ , but which may be gracefully indicated instead by  $F$  in commemoration of Faraday) deducible from the experiments of Kohlrausch and the more recent ones of Mascart, viz.  $0001048$  (§ 103, footnote, Part V.), the end result is attained that

$$JF = 41.555 \times 10^6 \times 0001048 = 4355.$$

Now  $4355 = 4410 \times 0.9875$ ; so that whilst the actual measurements of E.M.F. are reduced in the ratio  $0.9868$ , those deduced from heat-valuations must concurrently be reduced in the ratio  $0.9875$ , or almost exactly to the same extent. If  $J$  be taken  $= 41.5 \times 10^6$ , the reduction ratio becomes  $0.9862$  instead of  $0.9875$ . Hence it appears that in order to reduce to the values most consistent with the bulk of evidence at present extant the various E.M.F. determinations described in the previous portions of these researches, it will practically suffice to multiply them by  $0.987$ , *i. e.* to subtract  $1.3$  per cent. of their value, whether the figures be direct determinations of E.M.F. or deductions from calorimetric experiments.

It may further be noticed that when the value  $0.987 \times 10^9$  for the B.A. unit is taken, in consequence that of Clark's cell becomes  $0.987 \times 1.457 = 1.438$  volt; so that the mean value of the E.M.F. corresponding to the work done in electrolysing water, as directly determined in Part II. § 46, becomes  $1.4808 \times 10^8$  C.G.S. units, taking  $J = 41.555 \times 10^6$  instead of  $42 \times 10^6$ , as in Part II. The mean heat-valuation arrived at § 31, Part I., from the results of various experimenters employing the calorimeter, being 34100 gramme-degrees, the product  $34100 \times JF$  becomes  $34100 \times 4355 = 1.4850$ , which value exceeds  $1.4808$  by only  $0.29$  per cent., a quantity falling within the limits of probable error in the experiments ( $\pm 0.32$  per cent.). Inasmuch as from various causes a slight systematic error of defect necessarily attended the direct determinations, the final conclusion is warranted that these direct determinations are sensibly in accordance with the two propositions, firstly that the B.A. unit is actually only  $0.987 \times 10^9$ ; and, secondly, that Clark's cell has an E.M.F. of  $0.987 \times 1.457 = 1.438$  volt.

159. The experiments described in §§ 153 and 154 lead to the conclusion that a Daniell cell containing solutions of zinc and copper sulphate of equal strengths has an almost invariable E.M.F. whatever the strengths of the solutions when the plates are of amalgamated zinc and electro-copper ; but rises in E.M.F. if the plates are either amalgamated zinc and amalgamated copper, electro-zinc and electro-copper, or, *à fortiori*, electro-zinc and amalgamated copper. It seemed desirable to substantiate these deductions more rigorously. Accordingly two pairs of solutions of zinc and copper sulphate were carefully prepared, such that one pair had the composition 2·069  $\text{MSO}_4$  100  $\text{H}_2\text{O}$ , and the other the composition 0·937  $\text{MSO}_4$  100  $\text{H}_2\text{O}$ . Cells were then set up with these fluids, opposed to one another, and series of readings taken. It was found that the numbers thus obtained exhibited much greater divergences and fluctuations than those similarly obtained with cells where the molecular strengths of the solutions were not equal in each case respectively. In the latter case the current always passed in one direction, and did not exhibit any very marked alteration in magnitude during the first 15 to 30 minutes after setting up (during which period the observations above described were ordinarily made) ; but with two opposed Daniell cells, containing pairs of solutions of the same strengths in each severally, the differential current sometimes passed in one direction on first setting up, sometimes in the opposite direction ; sometimes it increased in intensity as time elapsed, and sometimes it diminished : in the latter case occasionally it diminished to *nil*, and then flowed in the opposite direction with gradually increasing intensity. Thus, for instance, the following numbers were obtained in one set of observations where the density never exceeded 0·02 microamperes per square centimetre, and was usually much less, so that "polarization" errors were eliminated (§ 150). The total resistance in circuit (including galvanometer and cells) was 107,400 B.A. units. The sign + indicates that the E.M.F. of the cell containing the stronger solutions was higher than that of the other ; the sign — indicates the opposite. Readings were taken every minute for 15 minutes after setting up ; the plates were then exchanged (after rinsing with the appropriate solutions), and another similar series of readings taken : a

second, and then a third exchange was similarly made, readings for 15 minutes being again taken in each case: the readings are translated into millivolts, every scale-division being equal, in these experiments, to  $85.7 \times 10^{-12} + 107,400 = 0.00000895$  volt = 8.95 microvolts.

Minutes after first setting up.	Before plates exchanged.	After first exchange.	After second exchange.	After third exchange.
1 .....	-1.3	-2.0	+4.5	+5.4
2 .....	-1.4	-2.0	+3.2	+3.4
3 .....	-1.5	-2.1	+2.1	+2.0
4 .....	-1.5	-2.1	+1.3	+1.0
5 .....	-1.5	-2.1	+ .7	+ .5
6 .....	-1.5	-2.2	+ .4	- .7
7 .....	-1.5	-2.2	+ .1	-1.3
8 .....	-1.6	-2.2	- .3	-1.7
9 .....	-1.6	-2.2	- .5	-2.0
10 .....	-1.6	-2.2	- .7	-2.2
11 .....	-1.6	-2.2	- .8	-2.4
12 .....	-1.6	-2.1	- .9	-2.5
13 .....	-1.6	-2.1	-1.0	-2.6
14 .....	-1.6	-2.1	-1.0	-2.7
15 .....	-1.6	-2.1	-1.0	-2.7
Average ...	-1.5	-2.1	+ .4	- .6
General average ..... = -0.9.				

In precisely the same way the following numbers were obtained in a duplicate experiment:—

During 1st minute.	-2.3	-1.1	+2.7	+3.4
During 8th minute.	-1.6	- .4	+1.4	+2.2
During 15th minute.	-1.3	- .1	+ .7	+1.2
Average of all observations.	-1.6	- .5	+1.5	+2.1
General average ..... = +.4.				

The mean of this and the preceding experiment gives  $-0.25$ , an amount evidently quite negligible in comparison with the fluctuations in the value of the net E.M.F. in operation in the several series of observations; and hence indicating that the E.M.F. of a cell set up with zinc- and copper-sulphate solutions of the same strength, amalgamated zinc and electro-copper,

*is really independent of the solution-strength within the limits of observational error.*

Using the same solutions in the same way the following values were obtained, showing that the E.M.F. really does rise perceptibly with the solution-strength when amalgamated copper is substituted for electro-copper, or when electro-zinc is substituted for amalgamated zinc:—

**Amalgamated Zinc and Amalgamated Copper.**

During 1st minute.	{	-·5	+15·3	+9·1	+13·0
During 8th minute.	{	-·7	+ 7·7	+1·3	+ 5·7
During 15th minute.	{	-·8	+ 5·2	0	+ 3·8
<b>Average of all observations.</b>	{	-·7	+ 9·0	+2·7	+ 6·5
General average .....					= +4·4.

**Electro-zinc and Electro-copper.**

During 1st minute.	{	-1·2	+6·3	+8·2	+7·2
During 8th minute.	{	+0·9	+4·0	+5·7	+4·4
During 15th minute.	{	+1·8	+2·9	+3·4	+3·5
<b>Average of all observations.</b>	{	+ ·3	+4·2	+5·6	+4·8
General average .....					= +3·7.

**Electro-zinc and Amalgamated Copper.**

During 1st minute.	{	+5·4	+6·9	+7·8	+11·1
During 8th minute.	{	+5·4	+5·5	+5·8	+ 8·0
During 15th minute.	{	+5·5	+4·3	+5·1	+ 5·8
<b>Average of all observations.</b>	{	+5·4	+5·5	+6·1	+ 7·9
General average .....					= +6·2.

*Heat developed during Intermixture of Solutions of Zinc (Copper or Cadmium) Sulphates or Chlorides of different Strengths.*

160. The results above described show that when two solutions of different strengths, but containing the same metallic salt, are allowed to intermix by diffusion, plates of the metal contained in the salt immersed in the two solutions respectively acquire different potentials, the potential-difference set up with any given pair of solutions being to some extent dependent on the surface-characters of the plates employed, but being, *ceteris paribus*, greater the greater the difference between the strengths of the solutions, the plates immersed in the stronger solution acquiring the higher potential. It is evident that if there is a development of heat during intermixture of the solutions used, the work done by a current developed on connecting the plates by a conductor may reasonably be supposed to be done in virtue of this heat-development, just as the work done by an ordinary voltaic couple is done in virtue of the heat developed by the chemical actions taking place therein. Accordingly it becomes of interest to determine precisely what amounts of heat are actually generated during intermixture in order to see what relationships hold between the electro-motive forces actually generated and those corresponding to the heat-developments.

The required "heats of intermixture" are readily calculable from the values representing the "heats of dilution" obtained by measuring the amounts of heat produced when solutions of metallic salts are diluted to known extents by means of water. If  $h_1$ ,  $h_2$ ,  $h_3$  respectively represent the heats of dilution of gramme-molecules of the three solutions  $\text{MSO}_4$ ,  $2a \text{H}_2\text{O}$ ,  $\text{MSO}_4 2b \text{H}_2\text{O}$ , and  $\text{MSO}_4(a+b) \text{H}_2\text{O}$  to the same further extent, then  $H$ , the heat produced by mixing a gramme-molecule of the first solution with one of the second so as to produce two of the third, is given by the equation

$$H = h_1 + h_2 - 2h_3.$$

In order to obtain the data for the calculation of the various values of  $H$  in the case of the solutions examined in the preceding pages, a number of calorimetric determinations were made, substantially in the way described by Julius Thomsen

(*Thermochemische Untersuchungen*, i. p. 18, 1882), using a calorimeter containing 1 litre of fluid in the lower compartment. The quantity of salt employed was usually close upon  $\frac{1}{7}$  grammie-molecule, the weight being arranged so that the resulting fluid was of the strength  $\text{MSO}_4 \text{ 400 H}_2\text{O}$ , or  $\text{MCl}_2 \text{ 400 H}_2\text{O}$ . The thermometers used were graduated in millimetres, about 11 millimetres representing  $1^\circ \text{C}$ .; so that readings being made to  $\pm \frac{1}{25}$  millim., the thermometer-error was  $\pm \frac{1}{22}$  of  $1^\circ \text{C}$ . As determined by means of various blank experiments (with water only intermixed), the limit of accuracy of each experiment was within  $\pm 10$  grammie-degrees; so that each observation might be erroneous within the limits of not exceeding  $\pm 70$  grammie-degrees per grammie-molecule; but as several observations were usually made and averaged, the probable error of each average was ordinarily within  $\pm 25$  grammie-degrees. The following numbers were ultimately obtained as means from upwards of fifty observations, indicating the heat-evolution, in grammie-degrees per grammie-molecule, on diluting  $m \text{ MSO}_4 \text{ 100 H}_2\text{O}$  to  $\cdot 25 \text{ MSO}_4 \text{ 100 H}_2\text{O}$ , or  $m \text{ MCl}_2 \text{ 100 H}_2\text{O}$  to  $\cdot 25 \text{ MCl}_2 \text{ 100 H}_2\text{O}$ . Plate V. fig. 6 represents the values graphically.

	Zinc sulphate.	Copper sulphate.	Cadmium sulphate.	Zinc chloride.	Cadmium chloride.
$m=25$ .....	.....	.....	.....	9000	
20.....	.....	.....	.....	8050	
10.....	.....	.....	.....	6100	
7.....	.....	.....	1450		
6.....	.....	.....	1075		
5.....	375	.....	825	4800	
4.....	175	.....	625	4400	
3.....	100	.....	450	3800	
2.....	50	50	275	2700	
1.5 }	Less than	Less than	200		
1 }	errors of	errors of	75	1250	
.5 }	observation.	observation.	.....	400	

161. On calculating from these figures the values of  $h_1$ ,  $h_2$ , and  $h_3$ , and hence those of  $H$ , for particular cases, it becomes evident that, as a general rule, the E.M.F. corresponding to the value of  $H$  falls below the potential-difference actually set up between two plates immersed in solutions of different strengths, the difference being sometimes very considerable. Thus the following tables represent the results thus calculated

when solutions  $\text{MSO}_4 2a \text{H}_2\text{O}$  and  $\text{MSO}_4 2b \text{H}_2\text{O}$  are intermixed so as to form  $\text{MSO}_4 (a+b) \text{H}_2\text{O}$  when  $b=200$ , and consequently when  $h_2=0$ . The "observed" values quoted are those obtained with electro-coated plates throughout, save in the case of zinc chloride, where amalgamated plates were employed; all the electromotive forces are expressed in millivolts.

Zinc Sulphate.							
2a.	a+b.	h <sub>1</sub> *	2h <sub>3</sub> .	H.	Corre-sponding E.M.F.	Observed E.M.F.	Excess.
20	210	375	0	375	8	27	19
25	212.5	175	0	175	4	22	18
33.3	216.7	100	0	100	2	17	15
50	225	50	0	50	1	13	12
100	250	0	0	0	0	8	8
Copper Sulphate.							
50	225	50	0	50	1	17	16
100	250	0	0	0	0	12	12
200	300	0	0	0	0	6	6
Cadmium Sulphate.							
16.7	208.3	1075	25	1025	23	34	11
20	210	825	25	775	17	28	11
25	212.5	625	25	575	13	23	10
33.3	216.7	450	25	400	9	18	9
50	225	275	25	225	5	14	9
66.7	233.3	200	25	150	3	9	6
100	250	75	20	35	1	4	3
Zinc Chloride.							
4	202	9000	790	8210	181	264	+83
5	202.5	8050	790	7260	160	225	+65
10	205	6100	780	5320	118	149	+31
20	210	4800	760	4040	89	65	-24
25	212.5	4400	750	3650	80	57	-23
33.3	216.6	3800	730	3070	68	52	-16
50	225	2700	700	2000	44	40	-4
100	250	1250	600	650	14	23	+9
Cadmium Chloride.							
20	210	100	0	100	2	32	30
100	250	0	0	0	0	14	14

Analogous results are obtained when the calculations are similarly made for other kinds of mixture: the observed E.M.F. generally notably exceeds that calculated from the heat of intermixture\*. It would hence seem that the *modus operandi* of a "diffusion-cell" is to some extent rather analogous to that of a thermo-couple than to that of an ordinary galvanic element, part at least of the energy gained outside the battery being due, not to the heat-development during chemical action taking place, but to the transformation of sensible heat into electric-current energy. It is noteworthy, moreover, that analogous phenomena are presented in cases where strong and weak solutions of acids (*e. g.* nitric and sulphuric) interdiffuse, platinum or other unoxidizable plates being employed: diffusion-cells of this kind are now being examined.

By uniting together in series a sufficient number of diffusion-cells, all the effects of an ordinary voltaic battery can be produced, at least those compatible with the presence of a large resistance in circuit: electrolysis of metallic solutions (*e. g.* copper sulphate) is readily brought about.

*Volume-alteration on Intermixture of Solutions of Zinc, Copper, and Cadmium Sulphates.*

162. Although not directly connected with the subject of electrical measurement of chemical affinity, it yet seemed of some interest to examine how far the volume-alterations that take place on mixing solutions of different strengths of zinc (copper or cadmium) sulphate run parallel with the thermal developments thereby caused. It might reasonably be anticipated that the much greater heat-evolution taking place on dilution of cadmium sulphate as compared with zinc or copper sulphate would be found to be concurrent with a greater amount of volume-alteration. On examining the matter, how-

\* Since these experiments were made, the third volume of Julius Thomsen's *Thermochemische Untersuchungen* has appeared; in this are given the results of this author's previously unpublished experiments on the heat of dilution of solutions of zinc and copper sulphates, and of zinc chlorides. These figures do not materially differ from those cited above; and their use, instead of those employed in this paper makes no noteworthy difference in the end conclusion that the heat of intermixture usually represents a less E.M.F. than that actually set up in any given case.

ever, this is not found to be the case ; the volume-alterations on dilution through a given range being but little different, whichever of the three sulphates be employed, in every case contraction\* taking place, even when the solution is already so far diluted as not to cause any measurable heat-evolution on mixing with water.

The observations were made with a large-bulbed dilatometer holding about 94 cubic centim. The volumes corresponding to the various graduations were determined by introducing a known weight of distilled water, and determining the level of the water in the stem—first, when the temperature was a little below 18°·5, the instrument being immersed in a large vessel of water kept agitated ; and secondly, when the temperature was a little above 18°·5. In this way the level at 18°·5 was obtained by interpolation. The weight of the contained water (reduced to a vacuum) being known, the volume in cubic centimetres occupied up to the level at 18°·5 was calculated by the formula  $V = \frac{W}{.998602}$  ; where V is the volume in cubic centimetres, W the weight *in vacuo*, and ·998602 the weight of 1 cubic centimetre in grammes at 18°·5 (Kopp). By making a series of such observations a capacity-table was calculated for the instrument, expressing the volume in cubic centimetres at 18°·5 for each graduation. A known weight of the solution to be diluted was then introduced, and the level at 18°·5 obtained by making observations a little below and a little above that temperature, so as ultimately to obtain the volume occupied by a given weight (reduced to vacuum) of solution. Repetitions of experiments gave values according together within a range of ·00003 (3 milligrammes in 94 cubic centim.), and often within much less ; the chief source of discrepancy being in the correction for reduction to a vacuum which was altogether about 100 milligrammes, necessarily varying with the temperature and barometric pressure, so that a small error in temperature or pressure estimation made several milligrammes difference in weight-correction.

\* The rough values obtained in § 106 (Part V.) led to the conclusion that on diluting zinc- or copper-sulphate solution with water an increment in volume takes place. This is now found to be incorrect, the experimental errors of the rough observations being greater than the volume-alterations to be measured.

On the whole, the probable error of the average of some three or four repetitions of an observation was less than  $\pm 0.00001$  (1 milligramme in 94 cubic centim.).

A quantity of the solution to be diluted was then weighed up in a stoppered bottle and a weighed quantity of water added, the weighings being reduced to a vacuum: the whole was thoroughly intermixed, and the weight of a cubic centimetre of the diluted fluid determined as before in the dilatometer; the contraction was then calculated by means of the formula

$$C = \frac{W}{s_1} + \frac{w}{998602} - \frac{W+w}{s_2};$$

where  $C$  is the contraction in cubic centimetres,

$W$  the weight (*in vacuo*) of solution diluted,

$w$  " " " of the water added thereto,

$s_1$  the weight at  $18^{\circ}5$  of 1 cubic centim. of the solution diluted.

$s_2$  the weight at  $18^{\circ}5$  of 1 cubic centim. of the dilute fluid produced.

The following numbers will serve as an example:—

Temper- ature.	Dilatometer reading.	Reading at $18^{\circ}5$ .	Cubic centim. corresponding from table of instrument.	Weight of fluid <i>in vacuo</i> .	Weight <i>in vacuo</i> of 1 cubic centim. at $18^{\circ}5$ *.
17.0	6.25	7.05	94.743	97.671	1.03090
19.7	7.70		94.556	97.467	1.03088
17.0	1.15	1.87	94.556	97.467	1.03088
19.3	2.25		94.556	97.467	1.03088
Mean .....					1.03089

\* In the course of these observations the following mean numbers were obtained, representing the weights *in vacuo* at  $18^{\circ}5$  C. of 1 cubic centim. of various solutions  $MSO_4 \cdot nH_2O$ :—

Copper sulphate.	Zinc sulphate.	Cadmium sulphate.
$n=44.8$ 1.18725	$n=19.06$ 1.41699	$n=15.81$ 1.59169
75.3 1.11325	19.31 1.41073	18.07 1.52829
109.9 1.078155	21.33 1.376055	18.10 1.52724
174.9 1.049195	32.3 1.25859	32.4 1.31285
276.4 1.03089	49.5 1.17310	49.4 1.21020
462.7 1.01805	98.8 1.088265	95.6 1.11082
	142.8 1.061275	162.9 1.06537
	219.1 1.03980	260.4 1.040795
	422.1 1.020215	424.4 1.02461
	466.0 1.01817	

This solution was made by mixing 53.781 grammes of copper-sulphate solution (of which one cubic centim. was similarly found to weigh 1.18725 gramme) with 232.509 grammes of water (all weights corrected to vacuum), whence

$$C = \frac{53.781}{1.18725} + \frac{232.509}{.998602} - \frac{286.290}{1.03089} = .422.$$

The solution diluted was found by analysis\* to contain 16.525 per cent. of anhydrous  $\text{CuSO}_4$ , corresponding with 2.231  $\text{CuSO}_4 \text{ 100 H}_2\text{O}$ ; hence there was employed altogether  $53.781 \times 16.525 = 8.887$  grammes of  $\text{CuSO}_4$ , or .0557 grammme-molecule; so that the contraction per grammme-molecule was  $\frac{.422}{.0557} = 7.58$  cubic centim., the diluted fluid possessing the composition .362  $\text{CuSO}_4 \text{ 100 H}_2\text{O}$ .

In precisely the same way the following values were obtained on diluting 2.231  $\text{CuSO}_4 \text{ 100 H}_2\text{O}$  to other extents:—

Solution ultimately obtained, $n \text{ CuSO}_4 \text{ 100 H}_2\text{O}$ .	Contraction in cubic centimetres per grammme-molecule.
$n = 1.328$	2.76
$= .910$	4.40
$= .572$	6.19
$= .362$	7.58
$= .216$	8.88

Similarly the following values were obtained on diluting 5.247  $\text{ZnSO}_4 \text{ 100 H}_2\text{O}$  to various extents:—

$n = 4.744$	0.96
$= 3.096$	4.78
$= 2.020$	7.59
$= 1.012$	11.23
$= .700$	12.63
$= .457$	14.03
$= .237$	15.69

And the following, on similarly diluting 6.325  $\text{CdSO}_4 \text{ 100 H}_2\text{O}$ :—

\* The mode of analysis adopted was to evaporate to dryness a weighed quantity of solution and weigh the residual anhydrous salt after continued heating to  $300^{\circ}$ – $400^{\circ}$ , terminating in very gentle ignition for a minute or two at a red heat barely visible in the dark.

Solution ultimately obtained, $n \text{ CuSO}_4 \text{ } 100 \text{ H}_2\text{O}$ .	Contraction in cubic centimetres per gramme-molecule.
$n = 5.534$	1.23
$= 3.086$	5.86
$= 2.024$	8.38
$= 1.046$	11.46
$= .614$	13.35
$= .384$	14.98
$= .235$	15.81

On graphical representation on a large scale and interpolation, the following values are deduced as the amounts of contraction taking place on diluting to the strengths  $.25 \text{ MSO}_4 \text{ } 100 \text{ H}_2\text{O}$  solutions of strength  $n \text{ MSO}_4 \text{ } 100 \text{ H}_2\text{O}$ :-

	Zinc sulphate.	Copper sulphate.	Cadmium sulphate.
$n = .25$	0	0	0
.5	1.8	1.85	1.75
1.0	4.25	4.5	4.0
1.5	6.35	6.4	5.95
2.0	8.0	7.95	7.4
2.25	8.65	8.55	7.95
3.0	10.8	.....	9.95
4.0	12.95	.....	11.95
5.0	15.05	.....	13.75
5.5	16.0	.....	14.5

The curves marked respectively 1, 2, and 3 (Pl. V. fig. 7) represent these values. It is evident that the contraction with cadmium solutions is always less than that with zinc- or copper-sulphate solutions, instead of greater, as might have been *a priori* anticipated from the greater heat of dilution. The difference, however, is in no case very great; whilst with zinc and copper solutions the curves almost coincide.

163. From these values the amounts of contraction on intermixture of gramme-molecules of two solutions of any one of the three salts differing in strength are readily calculable by the formula

$$C = c_1 + c_2 - 2c_3,$$

parallel with the analogous equation for heats of intermixture (§ 160); where C is the contraction on intermixture, and  $c_1$ ,  $c_2$ , and  $c_3$  respectively the contractions on dilution to the same ultimate limit of the solutions  $\text{MSO}_4 \text{ } 2a \text{ H}_2\text{O}$ ,  $\text{MSO}_4 \text{ } 2b \text{ H}_2\text{O}$ , and  $\text{MSO}_4 \text{ } (a+b) \text{ H}_2\text{O}$ ; and more generally still the contrac-

tions are calculable that ensue when any two solutions of any pair of the three salts are intermixed. Thus, when A gramme-molecules of  $\text{MSO}_4 \text{mH}_2\text{O}$  and B gramme-molecules of  $\text{M}'\text{SO}_4 \text{nH}_2\text{O}$  are intermixed, the resulting mixture is

$$\left\{ \begin{array}{l} \text{M} \\ \text{M}' \end{array} \right\} \text{SO}_4 \frac{mA + nB}{A + B} \text{H}_2\text{O}.$$

If, then,  $a$  be contraction per gramme-molecule on diluting the first solution to the strength of the mixture, and  $b$  be the (negative) contraction ensuing on (negatively) diluting the second solution to the same strength, the total contraction on intermixture is  $Aa + Bb$ , and the contraction per gramme-molecule of the two salts used jointly is  $\frac{Aa + Bb}{A + B}$ . A number of experiments were made which showed that the actual contraction observed was sensibly identical (within experimental error limits) with that calculated in this way, the values of  $a$  and  $b$  being deduced from the above table by interpolation. Thus the following values were obtained:—

#### Different Solutions of the same Salt mixed.

Stronger solution.....	$\text{CuSO}_4 \quad 47 \text{H}_2\text{O}$	$\text{ZnSO}_4 \quad 19\cdot3 \text{H}_2\text{O}$	$\text{CdSO}_4 \quad 15\cdot81 \text{H}_2\text{O}$
Weaker solution .....	$\text{CuSO}_4 \quad 163 \text{H}_2\text{O}$	$\text{ZnSO}_4 \quad 148 \text{H}_2\text{O}$	$\text{CdSO}_4 \quad 171 \text{H}_2\text{O}$
Observed contraction	1.12	3.84	4.88
Calculated ,,"	1.13	3.83	4.66
Difference .....	+ .01	- .01	- .22

#### Solutions of different Salts used.

Stronger solution.....	$\text{ZnSO}_4 \quad 19\cdot3 \text{H}_2\text{O}$	$\text{CuSO}_4 \quad 47 \text{H}_2\text{O}$
Weaker solution .....	$\text{CuSO}_4 \quad 163 \text{H}_2\text{O}$	$\text{ZnSO}_4 \quad 148 \text{H}_2\text{O}$
Observed contraction ...	4.37	.92
Calculated ,," .....	4.23	.99
Difference .....	- .14	+ .07
$\text{CdSO}_4 \quad 15\cdot81 \text{H}_2\text{O}$	$\text{CdSO}_4 \quad 15\cdot81 \text{H}_2\text{O}$	$\text{ZnSO}_4 \quad 19\cdot3 \text{H}_2\text{O}$
$\text{CuSO}_4 \quad 163 \text{H}_2\text{O}$	$\text{ZnSO}_4 \quad 148 \text{H}_2\text{O}$	$\text{CdSO}_4 \quad 171 \text{H}_2\text{O}$
4.39	4.19	4.41
4.36	4.11	4.42
- .03	- .08	+ .01

Since but little difference exists between the contractions on dilution through given ranges, whether zinc, copper, or

cadmium sulphate be employed, it results that the amounts of contraction on intermixture when two different solutions of the same salt are mixed will not differ greatly whichever of the three salts be employed. It would hence seem that there is a much closer connexion between the amount of contraction taking place on intermixture, and the potential difference thereby developed, than there is between either of these values and the heat-evolution simultaneously taking place. For varying solution-strengths, the first two values alter fairly concurrently and to extents not widely different, whether zinc, copper, or cadmium sulphate be used. But this is by no means the case with the heat-values, the cadmium value largely exceeding the corresponding zinc and copper values, which latter two are substantially identical.

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## IX. *On an Integrating Anemometer.*

By WALTER BAILY, M.A.\*

[Plates VI. & VII.]

ON June 10th, 1882, I communicated to the Society a design for an integrating anemometer, and exhibited a working model†. I have now to describe the instrument itself, which I have had made by Messrs. Elliott, with the assistance of a grant from the Royal Society. The mechanical part of the instrument is seen in perspective in Plate VI. fig. 1. The base is of iron, and the rest of the instrument is chiefly of brass. On the base stand four columns C, of which only two are shown in fig. 1. These hold a table O, of which fig. 2 gives a view as seen from above. The tops of the columns C are seen in fig. 2. The table supports four columns, D, of which only two are shown in fig. 1, and of all of which the positions are shown in fig. 2. The pillars D hold the supports of a spindle A, fig. 1, which is to be connected with a vane. There is another spindle, B, which is to be connected with Robinson's cups, and which turns, by means of cogs, the large horizontal disk X, so that X will revolve with a velocity which may be taken as proportional to that of the wind. The

\* Read December 8, 1883.

† Phil. Mag. Sept. 1882; Phys. Soc. Proc. vol. v. p. 157.

spindle A carries a horizontal bar G, which is to be kept by the vane in the direction of the wind, and which, by means of a forked end, holds a vertical pin rising from the centre of the bar F. This bar is pivoted at E to the centres of two trucks H, each of which runs by means of five wheels U between tram-lines M placed so as to form a cross with the arms directed towards the cardinal points (compare figs. 1 and 2). The centre of the cross is vertically over the centre of the disk X. Centrally between the tram-lines M are slits S through the table O. The object in having five wheels U placed as shown in fig. 1 (see also fig. 3) is to enable each wheel of the truck H to pass over the slits S, and yet always to keep the pivot E well within the base formed by the remaining four wheels, so that it may be perfectly steady. On the underside of the table O are similar tram-lines, N; and trucks K run in these tram-lines, each on five wheels, V. Fig. 3 shows one of these trucks seen from below, with portions of the tram-lines N.

Fig. 4 is an elevation showing an end view of the trucks H and K, with a portion of a section of the table O across a slit S. Two rods, T, of which the ends are shown in fig. 3, and of one of which a side view is shown in fig. 4, are rigidly connected with H and pass through the slit S and through holes in K. Spiral springs surrounding the rods T and resting on the heads of the rods press K upwards, and make it keep its position exactly and firmly under H. Each truck, K, carries firmly fastened to it two pieces of brass, L (see figs. 1, 3, 4); and between these pieces is pivoted a bar with arms J, and between these arms is pivoted a wheel W, which is carried in a vertical position also at right angles to the slit through which T passes. A rod I connected with K is surrounded by a spiral spring which presses on J, and so keeps a steady pressure between the wheel W and the disk X. The pivots of J and W are so placed that, when W touches X, these pivots all lie in one horizontal plane, and the point of contact of W with X is vertically below the centre of the pivot E (figs. 1, 2).

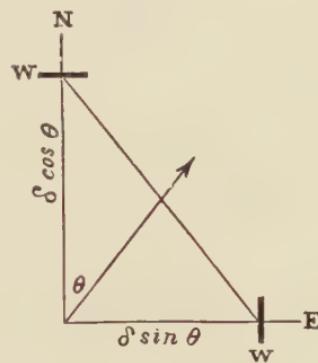
Now suppose the wind to lie between North and East, and the direction from which it blows to make an angle  $\theta$  with North. Let  $\Omega$  be the velocity of the wind. Then the resolved parts of the wind towards North and East will be  $\Omega \cos \theta$  and

$\Omega \sin \theta$  respectively. But if  $\delta$  be the length of the bar F (fig. 2) measured between the centres of its pivots E, it is easily seen, from the diagram in the margin, that the distances of the wheels W from the centre of the disk X (fig. 1) are  $\delta \cos \theta$  and  $\delta \sin \theta$  towards the North and East respectively. Now the speeds of the wheels W are proportional to the speed of the disk X on which they roll multiplied by these distances, and the speed of the disk X is proportional to the velocity  $\Omega$  of the wind. Hence the speeds of the wheels W are proportional to  $\delta \cos \theta \cdot \Omega$  and  $\delta \sin \theta \cdot \Omega$  respectively ; that is, they are proportional to  $\Omega \cos \theta$  and  $\Omega \sin \theta$ , which are the resolved parts of the velocity of the wind.

If, now, we were to add a mechanical counter to each of the wheels W, the increase of the readings of these counters would give the integral of the resolved parts of the wind towards the North and East ; and inasmuch as the wheels W revolve in the contrary direction when they have passed across the centre of the disk X, South winds would act on the counters as negative North, and West winds as negative East. Two counters would be sufficient, as a preponderance of South wind would be indicated by a decrease in the reading of the North counter, and a preponderance of West wind by a decrease in that of the East counter.

It was found, however, much more convenient to make each wheel W complete an electric circuit at each revolution, and to use an electric counter; but inasmuch as such a counter will not distinguish in which direction the wheel is turning, it was necessary to have separate counters for North and South, and to shunt the circuit from one counter to the other as the wheel W crossed the centre of the disk X, and to make a similar arrangement for East and West.

I will now describe the electric system adopted:—Parallel with the tram-lines M (fig. 2) are insulated rails R, one of which is seen in section in fig. 4. Each rail, R, is connected



by an insulated wire with an insulated binding-screw  $\sigma$ . Each truck, H, bears a thin insulated plate of brass, P, seen in face in fig. 2 and edgeways in fig. 3; and each end of the plate P carries a small wheel, Q. At any moment, except when the truck is passing the centre of the cross, one of the wheels Q rests on a rail R, and the other is in the air. This is clearly seen in fig. 4. At the moment when one of the trucks H (say the North and South one) passes, say, from North to South across the centre, the wheel Q on the North rail R runs off it, and the other wheel Q runs on to the South rail R, so that the plate P of the truck is always in electrical connexion with the binding-screw  $\sigma$  belonging to the cardinal point towards which the truck lies. The rails R have for their upper edge a thin rail of platinum. This was added to the broad rail of brass, as it was found that points of dust or corrosion sometimes made accidental breaks in the electrical contact between R and Q. In the truck K which runs below H are two parallel tongues Y, Z, very near one another (see fig. 3, in which the full length of Y is seen, but only the end of Z). Both are fixed to J; but Z is also insulated from J, and is connected by an insulated wire, which passes through the slit S (fig. 4) and through a hole in H, with the insulated plate P. The tongue Y is electrically connected with K, and so through various points of contact with the table O. There is a projection from the axle of the wheel W (fig. 3), which once in every turn of the wheel pushes against the tongue Y and brings it into contact with the tongue Z. On the table O (fig. 2) is another binding-screw  $\rho$ , which is not insulated. Now suppose a truck H to be upon the North arm of the cross. Its tongue Z is in electric connexion with the North binding-screw  $\sigma$ , and the whole of that part of the system is insulated from the table O. Every time the wheel W turns round, contact is made between Y and Z; and the effect is that the North  $\sigma$  is put into electrical connexion with the table O, and therefore with the binding-screw  $\rho$ . The general electrical system is shown in Plate VII., which gives a front view of the box of counters, and a diagram of the anemometer, batteries, and wires. The box contains four counters lettered according to the cardinal points, and from the binding-screws on one side (the right in the figure) insulated wires pass to the corresponding insulated binding-screws  $\sigma$  on the

anemometer. From the binding-screws on the other side of the box of counters insulated wires also proceed. The North and South wires are connected with one pole of a battery, and the East and West wires are connected with the same pole of a similar battery. The other poles of the batteries are connected by a wire which returns to the anemometer to the un-insulated binding-screw  $\rho$ . If more convenient, the return wire may of course be omitted, and the batteries and anemometer be connected to earth.

Let us now suppose the wind is blowing from about North-east. The trucks H, K are now on the North and East arms of the cross. The circuit through the South counter is complete from the tongue Y through the table O, the return wire, the South counter, and then to the South binding-screw  $\sigma$  and South insulated rail R; but there it stops, and no current can therefore pass through the South counter. The west circuit is stopped in a similar manner. But in the case of the other circuits, the insulated rail R is in contact with the wheel Q, and so through P the circuit is carried on as far as the tongue Z. Hence in the circuits through the North and East counters a current passes whenever the corresponding tongues Y and Z are pressed together, and the corresponding counter marks *one*.

To determine the value of the readings of the counters, we may resort to measurements of the instrument or to direct experiment. If we place one truck at its furthest distance from the centre and rotate the spindle B a certain number of times, and then note the increase in the reading of the corresponding counter, there will be found a constant ratio  $k$  between them, so that an increase of  $n$  on the counter denotes  $kn$  revolutions of B.

Letting  $\delta$ , as before, be the length of the bar F between its points E (fig. 2),  $\delta$  is the greatest distance which the wheel W can go from the centre. Put  $\epsilon$  for the radius of W,  $\zeta$  for the number of cogs on the edge of the disk X, and  $\eta$  for the number of cogs on the spindle B; we have

$$\text{Speed of X : speed of B} = \eta : \zeta,$$

$$\text{,} \quad \text{W:} \quad \text{,} \quad \text{X} = \delta : \epsilon,$$

$$\text{,} \quad \text{W:} \quad \text{,} \quad \text{B} = \delta \eta : \epsilon \zeta = 1 : k,$$

which gives us  $k = \frac{\epsilon \zeta}{\delta \eta}$ .

If we place the arm G in any other position and turn the spindle B for some time, and then read  $p$  and  $q$  as the increase in the readings of the counters of the adjacent cardinal points, the resultant reading for magnitude is  $\sqrt{p^2+q^2}$ , and the number of revolutions of B will be  $k\sqrt{p^2+q^2}$ , where  $k$  has the same value as before. The direction of the bar G may be determined by taking  $\theta$  as the angle between the bar and the cardinal point to which  $p$  relates. Then

$$p : q = \cos \theta : \sin \theta;$$

whence

$$\tan \theta = \frac{p}{q}.$$

Of course if B is rotated a certain number of times (say 500), the value of  $\sqrt{p^2+q^2}$  must be the same in whatever position G has been fixed throughout the experiment.

By repeating this experiment with different positions of G, we get a means of testing the amount of error to which the instrument is liable.

When the anemometer is connected with a vane and with Robinson's cups, let us suppose the wind to remain in one direction for some time; or, if that cannot be secured, let us either tie up the vane, or disconnect it from the spindle A and fasten the spindle. Let  $l$  revolutions of the cups indicate one mile of wind, and  $m$  revolutions of the cups give one revolution of the spindle B. Let  $p$  and  $q$  be the readings of the counters, then the miles of wind indicated will be

$$k\sqrt{p^2+q^2} \cdot \frac{l}{m}.$$

In ordinary use the bar G will be shifted about in all directions by the wind, and we may have an increase in the readings of all the counters; let these be represented by  $n$ ,  $s$ ,  $e$ ,  $w$  for North, South, East, and West respectively; then the resultant transfer of air during the interval since the last reading will be

$$k\sqrt{\{(n-s)^2+(e-w)^2\}} \frac{l}{m};$$

and its direction measured from North towards East will be given by the equation

$$\tan \theta = \frac{e-w}{n-s}.$$

X. *On a Modified Resistance-Balance.*By Professor SILVANUS P. THOMPSON, *B.A., D.Sc.\**

[Plate VIII.]

SEVERAL forms of Resistance-Balance modified for the purpose of facilitating the accurate measurement of small resistances or small differences of resistance are known. The modification due to Prof. Fleeming Jenkin †, and the Double-bridge of Sir W. Thomson ‡ are perhaps the earliest and least-known of these. Kirchhoff's arrangement, as further modified by Matthiessen, is well known under the name of the "divided-metre" bridge. The method of using this form of balance suggested by Professor G. Carey Foster §, in which the difference between two nearly equal resistances is expressed directly in terms of a length of a graduated wire whose resistance is very accurately known, is so extremely reliable, that probably no one who once adopts this method of testing resistances will ever go back to the cruder and less accurate methods. The essence of the method lies in arranging the coil whose resistance is to be measured and the standard coil to which it approximates in series with the graduated wire, in such a manner that the positions of the two coils can be interchanged. The points of the wire at which the potential is the mean between the potentials at the two ends of the series having been determined, both before and after the interchange, the resistance of the length between these two points is the desired difference. A special modification of the balance for facilitating Foster's method was described to the Physical Society in Dec. 1879 by Dr. J. A. Fleming ||; and has been since then systematically used in the Cavendish Laboratory by the Committee on Electrical Standards for the comparison of standard coils. Although extremely convenient, Dr. Fleming's Balance appears to me to be open to several objections. In the first place, the interchange of

\* Read February 23, 1884.

† Report of Committee on Electrical Standards.

‡ Proc. Roy. Soc. vol. xi. p. 313 (1861).

§ Proc. Soc. Telegr. Engin. vol. i. pt. 2, p. 196 (1872).

|| Proc. Phys. Soc. vol. iii. p. 174; Phil. Mag. ser. 4, vol. ix. p. 109 (1880); Telegr. Journal, vol. viii. p. 3 (1880).

the two coils, though much more easily accomplished than in the older divided-metre form, is effected by lifting the terminals of each coil out of one of two pairs of mercury-cups, and removing them to the other pair. This operation is not convenient in certain cases, as, for example, when the resistance is being taken of a wire heated in an oil-bath to various successive temperatures, or when some contact-resistance is to be measured which must on no account be shaken. Again, in Fleming's Balance the graduated wire is bent into a circle and laid in a groove, contact being made by a trigger attached to an arm, pivoted at the centre of the circular wire. This arrangement, though I have heard no complaint of its practical efficiency, is open to two objections. It must be much more difficult to lay the wire with an even stress at all points than is the case with a straight wire stretched between two points. The range of resistances measurable by this bridge is limited to something less than the actual resistance of the graduated wire. Lastly, a circular scale having about  $300^{\circ}$  divided into 1000 parts is not so easily obtained as a straight metre-scale.

I have therefore designed a form of resistance-balance which meets the desiderata. It consists of two parts—a divided wire or rheocord, and an arrangement of mercury-cups, connecting-pieces, and terminals to be attached at the back of the rheocord part. The figure 1, Plate VIII., shows the general arrangement of these two parts; the connexions between the two parts being made by strips of copper 3 millim. thick, secured under clamping-screws. X is the coil whose resistance is to be measured, and S the standard coil. The terminals of each of these coils dip into two large mercury-cups turned in solid copper; these are shown half size in fig. 2, and are marked  $m\ n$  and  $m'\ n'$  respectively. Between these cups lie four parallel bars of solid copper  $a\ a'$ ,  $b\ b'$ ,  $c\ c'$ , and  $d\ d'$ , the ends of which terminate also in mercury-cups. The bars  $a\ a'$  and  $b\ b'$  communicate by stout copper connexions with the two ends of the rheocord part. The other two bars communicate with the battery terminals and with the terminals for the two balanced coils A and B. In all accurate tests these coils should be approximately equal to the X or S, and should be very nearly equal to one another.

As they are not required to be interchanged, they are simply clamped with copper connexions under flat-headed terminal screws. Short stout pieces of copper, amalgamated at the ends, serve to connect the mercury-cups as shown in fig. 1,  $m$  being connected with  $a$ ,  $n$  with  $d$ ,  $m'$  with  $b'$ , and  $n'$  with  $c'$ . The connexions being thus made, an observation is taken, and the distance  $x$  along the scale of the point of contact with the galvanometer-circuit is recorded. Then the connexions are altered,  $m$  being placed in communication with  $b$ ,  $n$  with  $c$ ,  $m'$  with  $a'$ , and  $n'$  with  $d'$ . This has the same effect as if  $X$  and  $S$  were bodily interchanged ; and without lifting either of those coils as in Fleming's instrument. Balance having been once more obtained, and a new reading  $x'$  of the scale having been taken, the length  $x - x'$ , multiplied by the resistance per centim. of the divided wire, is equal to the actual difference between  $X$  and  $S$ .

The switch-board part is made of such dimensions that it can be attached on to any of the ordinary pattern of metre-bridges. The ordinary metre-balance is, however, limited in its application, so far as Foster's method of comparison is concerned, to the comparison of resistances which do not differ by a greater amount from one another than the actual resistance of the wire of the rheocord part. To facilitate the comparison of coils of high resistance whose resistances differ by several ohms, I have adopted the following arrangement of the rheocord part. Two wires are selected, each two metres long, one having a resistance of about a quarter of an ohm, the other from eight to ten ohms. They are stretched parallel upon a board 213 centim. in length, provided with a two-metre scale, which should be divided into millimetres. Either of these wires can be used at will, connexion being made to either at one end of the bridge by a stout copper link dipping into mercury-cups drilled in the wood and lined with copper. Stout copper rods of about 1 square centim. section lead from the ends of the stretched wires to the screws, by which the switch-board part is connected with the rheocord part. The galvanometer-contact is made by means of a sliding key shown separately in fig. 3, which is provided with a vernier, and which by a simple arrangement can be set so as to make the contact with either

the thick or the thin wire, as may be desired. In the instrument exhibited to the Society the stout wire is of german-silver 2·1 millim. in diameter, and of 0·2385 ohm resistance. The thin wire is of silver-platinum alloy; its diameter is 0·33 millim., and its resistance 8·21 ohms. The form of slider adopted is a much more well-conditioned arrangement than the usual heavy medal sliding key standing on three legs, and is more convenient in practice. The greater length of rheocord, though it renders the instrument less portable, increases the range of the instrument without affecting its sensitiveness.

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## XI. *On Eutexia.* By FREDERICK GUTHRIE\*.

### VII.

**INTRODUCTION.**—Although this memoir does not treat directly of the relationship between water and salts, the subject is so analogous with that examined in my memoirs on “Salt-Solutions and Attached Water,” that I have numbered the paragraphs in sequence with those of memoir VI. on that subject (Proc. Physical Society, vol. ii. p. 291).

The main argument of the present communication hinges upon the existence of compound bodies, whose chief characteristic is the lowness of their temperatures of fusion. This property of the bodies may be called Eutexia †, the bodies possessing it eutectic bodies or eutectics ( $\epsilon\nu\tau\eta\kappa\epsilon\iota\nu$ ). It is at once apparent that the cryohydrates are essentially eutectic. It will, however, perhaps be better to make the term more useful by limiting its application. I shall use it, and I should like it to be used by others, for bodies made up of two or more constituents, which constituents are in such proportion to one another as to give to the resultant compound body a minimum temperature of liquefaction—that is, a lower temperature of liquefaction than that given by any other proportion. Here, again, the cryohydrates completely satisfy the definition. But it will be shown that they constitute only one term of

\* Read May 24, 1884.

† Used in very much this sense by Aristotle. I should have preferred the word hypolytic; but I am instructed that, although sanctioned by its use in Chemistry, this employment of  $\nu\pi\sigma$  is not strictly admissible.

a series ; that their melting or liquefaction is quite continuous with the so-called fusion of mixed metals or salts ; and that the eutectic alloys of metals, many of which have been long imperfectly known, and the eutectic alloys of salts, which I shall describe (§§ 207-229), are the perfect homologues of the cryohydrates. Let me, in a word, invite my readers, while looking upon water as fused ice, to trace the analogy between the behaviour towards solids of water on the one hand, and some other fused substance on the other.

*Eutectic Metallic Alloys.*

§ 195. Metals mix with one another in various proportions forming Alloys, many of which are in extensive use in the arts. Amongst the most instructive aspects of alloys is certainly that which results from a comparison of the properties of the alloy with those of its constituents. And, further to specialize, the discussion of the relation between the temperature of fusion of the mixed metal and the temperatures of fusion of its elements forms a chapter of the highest significance.

§ 196. In studying this chapter, I employ Bismuth as one of the elements on account of its low melting-point, and because it can be got very pure. Fused bismuth will be the homologue of the water or fused ice of my previous memoirs, and the metal with which it forms alloys will be the homologue of the salt. The bismuth used in the following experiments melted at  $263^{\circ}$  C.

§ 197. *Bismuth and Zinc.*—It has been asserted that when bismuth and zinc are melted together two alloys are formed which do not mix, the upper being an alloy of 2·4 bismuth and 97·6 zinc, and the lower of from 8·6 to 14·3 bismuth and from 91·4 to 85·7 zinc (see § 206). Such a condition and such a ratio may accidentally exist ; but is only occasional. Let bismuth be fused and heated to about  $350^{\circ}$ , and let as much melted zinc be added in small quantities at a time as the bismuth will form a liquid alloy with at about that temperature. Let now the temperature be watched until it has sunk to about  $250^{\circ}$ . The liquid is run off and a little bismuth is added to the contents of the crucible, which is heated until fusion ensues, and a second amount of liquid at  $250^{\circ}$  is again obtained. This and the quantity obtained by the first process

are melted together and allowed to cool gradually. The temperature sinks almost immediately to  $248^{\circ}$ , and remains constant at that temperature. The alloy maintains the same temperature to the very last, and is the eutectic alloy of these metals. It showed on analysis :—

	Melting Per cent. temperature.
Bi . . . . .	92.85 }
Zn . . . . .	7.15 }

Of course this eutectic alloy is now to be made by melting the metals together in the above ratio ; but on account of the oxidation of the zinc at about its melting-point, it is better to provide a little excess of that metal and to remove the excess by the above method.

§ 198. *Bismuth and Tin*.—In forming the eutectic alloy of these, the bismuth need be only just fused. A roll of tin foil is stirred into the bismuth, and in spite of the cooling effect, the alloy which is formed remains liquid. When the temperature reaches about  $150^{\circ}$ , the roll of tin is withdrawn, and the temperature is watched as the alloy cools. The temperature ceases to fall at  $133^{\circ}$ , which is the fusion temperature of this eutectic alloy. Having satisfied oneself of this, the whole may be remelted, and about a quarter having been allowed to solidify at  $133^{\circ}$ , the rest is poured off, and is pure. This alloy is very finely crystalline when quickly cooled ; it is very brittle and its freshly broken surface closely resembles that of cast iron. It showed on analysis :—

	Temperature Per cent. of fusion.
Bismuth . . . . .	46.1 }
Tin . . . . .	53.9 }

§ 199. *Bismuth and Lead*.—Proceeding in a very similar manner as with tin, a fixed temperature of  $122^{\circ}7$  is reached. This eutectic alloy has the composition :—

	Temperature Per cent. of fusion.
Bismuth . . . . .	55.58 }
Lead . . . . .	44.42 }

It is of a bluish grey, is malleable and easily cut or sawn.

§ 200. *Bismuth and Cadmium*.—On adding melted cadmium to melted bismuth and proceeding as above, it is possible to obtain an alloy whose melting-point is  $144^{\circ}$  C. It shows, on analysis, the following composition :—

	Per cent.	Temperature of fusion.
Bismuth . . . . .	59.19	$144^{\circ}$
Cadmium . . . . .	40.81	

§ 201. So that we have the following results :—

Eutectic alloy of Bismuth with

Lead	contains	Per cent.	and melts at	$122.7^{\circ}$
Tin	„	53.90 tin	„	133
Cadmium	„	40.81 cadmium	„	144
Zinc	„	7.15 zinc	„	248

These weight-ratios are none of them simple atomic weight-ratios. Of course, in many cases, metals can be fused together in simple multiples of their atomic weights, but in most such cases, on cooling the alloy, one of the metals will separate out first and so destroy the ratio. In other cases an alloy richer than the original alloy in regard to one of the metals, and therefore a homologue of a subcryohydrate, separates, and the original ratio is again disturbed. When we are dealing with metals which, like antimony or arsenic, on the one hand, are themselves halogenous, or with such strongly chemico-positive metals as sodium on the other, we may and do get alloys of atomic composition—metallo-metallic salts. But the temperatures of fusion of these are never, as far as I am aware, lower than that of either (both) of the constituents. They are not eutectic. Nor is it easy to see any reason whatever why they should be so. On the contrary, we should expect such an alloy to be soluble in one or other of its elements, with depression of temperature. The statement therefore that alloys of minimum melting-points are got on mixing the metals in certain simple ratios of their atomic weights, is presumably to be put on one side. As the cryohydrate forms itself when a salt-solution of any strength loses heat, so the eutectic alloy forms itself when an alloy whose constituents are in any ratio is cooled. The only exception to this is when the constituents

are in the ratio homologous with that between the constituents of the subcryohydrate. So-called "fusible alloys," or "fusible metals," are imperfect eutectic alloys. And it is seen that the melting-points obtained by previous experimenters with bismuth-tin and bismuth-lead are considerably higher than those above shown (see also § 206).

§ 202. Further, if we take the eutectic alloy of bismuth-tin and that of bismuth-lead, and treat them together as though they were single metals, we get the eutectic alloy of the three metals ; or either of these alloys with bismuth-cadmium gives a corresponding tri-eutectic.

These and certain other tri-eutectic alloys may form the substance of a further communication. They stand in the closest connexion with the cryohydrates of mixed salts, which were discussed in §§ 109-116.

§ 203. Again, a tetra-eutectic is obtained either by building up from the tri-eutectic and a metal, or from three eutectics ; or perhaps more readily, although with greater waste of metal in the first tentative experiment, by fusing the four metals together. The three eutectic bismuth alloys above described were fused together in considerable quantity and in indefinite ratio. As the mass had only partly solidified at 100°, it was pressed in a linen bag under boiling water. The liquid portion was further cooled. A large amount remained liquid at 71° C. ; at which temperature the thermometer thenceforth stood until the whole was solid. On remelting several times, and collecting that which remained liquid after about a fifth had solidified, the eutectic alloy of bismuth-tin-lead-cadmium was obtained pure. It showed the following composition:—

Bismuth . . . . .	47.45	47.38
Lead . . . . .	19.39	19.36
Cadmium . . . . .	13.31	13.29
Tin . . . . .	20.00	19.97
	—	—
	100.15	100.00

The question, very interesting to mineralogists, immediately arises, Can a tetra-eutectic alloy be made without loss by mixing three dieutectic alloys in some proportion with one another ? The answer is in this case certainly in the negative.

For according to § 199, 19.36 of lead require 24.25 of bismuth. Again, according to § 200, 13.29 of cadmium require 19.27 of bismuth, and according to § 198, 19.97 of tin require 17.08 of bismuth. So that to satisfy the three metals lead, cadmium, and tin eutectically, 60.52 of bismuth would be required, instead of 47.45.

The above alloy is extremely closely grained and brittle. It may, however, be bruised and rolled. It takes a high polish. When in some thickness its fracture is conchoidal, exposing steel-grey surfaces. This highly eutectic alloy may find uses in the arts, as with the exception of alloys containing mercury and those of potassium and sodium, it has a melting-point lower than any alloy before described.

§ 204. The above experiments, in which bismuth replaced the ice of my previous experiments with salt-solutions and some other metal replaced the salt, are of course only a few of an innumerable series of series. But they will serve to show the genesis of bodies of this class. I have already\* pointed out how the "de-leading" of the lead-silver alloy in Pattinson's process is really analogous to the separation of ice from a salt-solution. The residual liquid alloy should have a composition analogous to that of a cryohydrate, and should be the eutectic alloy of lead-silver. If this be so, its temperature of fusion should be lower than that of lead itself; and that it is so is proved by the separation of solid lead from the melted mass. It is well known that Pattinson's process may be "pushed too far." According to the above interpretation, this simply means that when the fusion-temperature of the eutectic alloy is reached, this body solidifies as a whole and is raked away as the lead had been. A pyrometer, an air thermometer, in the mass would be an absolutely trustworthy guide as to the proper time for cupellation to replace "de-leading."

§ 205. That certain metals may and do unite with one another in the small multiples of their combining weights may be conceded. To such bodies the eutectic alloys bear the same relationship as the cryohydrates bear to the common hydrates, and, like the latter bodies, their constituents are not in the ratio of any simple multiples of their chemical equiva-

\* R. Inst. Lecture, Feb. 16, 1877.

lents. But their composition is not, on that account, the less fixed, nor are their properties the less definite. Many of these eutectic alloys have been known in partial purity for ages, having been nearly reached by repeated trial or by assuming a molecular ratio. But they have not been recognized as a class numbering merely as dieutectics several hundred (say 1700), which can be obtained, as above shown, systematically and in a state of great purity. Nor does the fact that several instances are known in which metals combine with one another in the chemical sense—that is, in simple multiple ratio by weight of their combining weights and with liberation of heat—at all diminish the possible number of such eutectic alloys. For, firstly, as a salt may unite with water, as when anhydrous chloride of calcium does so, to fix the water as crystalline water, and also may unite with water as a cryohydrate, so two metals may unite in one proportion while they form a definite eutectic alloy in another. Secondly, the very bodies resulting from the chemical union of the two metals will possibly, and probably, furnish starting-points of new series of eutectic alloys, consisting of a single metal on the one hand and the chemical alloy on the other.

§ 206. It will be instructive to compare the results given above with results obtained by some previous experimenters who have examined bismuth alloys.

According to Rose, one part by weight of lead, one of tin, and two of bismuth melt at  $93^{\circ}75$ . That a part of it may melt, and so the whole soften at that temperature, need not be questioned. But that the whole should melt from first to last at any fixed temperature, is so highly improbable as to be practically impossible on account of the simplicity of the proportion.

According to Matthiessen and v. Bose zinc and bismuth form two alloys, one containing 97.6 of zinc, and the other from 8.6 to 14.3 (instead of 7.15), which two alloys are immiscible. The melting-points do not appear to have been given. Indeed, as neither of these is eutectic, so neither has a proper melting-point.

The nearest approach to an eutectic alloy appears to have been made by Rudberg, who, on melting together 177 parts by weight of tin, and 213 of bismuth (tin = 45.38 per cent., bismuth = 54.62 per cent.), obtained an alloy which is said

to have a constant melting-temperature of  $143^{\circ}$ . Rudberg further states that all other ratios have higher melting-points, and that, on cooling, the liquid portion reduces itself to this ratio. The above ratio is intended for that between three "atoms" of tin and two of bismuth. For if the atomic weight of tin be 118 and that of bismuth 210 (Rudberg takes tin 56, bismuth 106.5), we should have in  $\text{Sn}_3\text{Bi}_2$  the percentage, tin = 45.74 per cent., bismuth = 54.26 per cent. It has been shown above that the true eutectic alloy has a melting-point  $10^{\circ}$  lower than Rudberg's, and the composition, tin = 53.9, bismuth = 46.1 per cent.

Again, it is stated that when lead and bismuth are fused together, in the proportion of three atoms of lead to two of bismuth, an alloy is obtained whose melting-point is constant at  $129^{\circ}$ . This ratio requires lead 42.49, bismuth 57.51 per cent. The true eutectic alloy has a melting-point  $6^{\circ}3$  C. lower, and, as we have seen, has the composition, lead 44.42, bismuth 55.58.

The preconceived notion that the alloy of minimum temperature of fusion must have its constituents in simple atomic proportion,—that it must be a chemical compound,—seems to have misled previous investigators. Such misconception could scarcely have arisen if the existence and properties of the cryohydrates had been known.

§ 206 A. It was shown many years ago (about 35) by my brother Francis, that if two counties are only then supposed to be in contact when they have linear common boundary, to colour a map so that no two counties in contact shall be coloured alike, four colours at most are needed. Taking the special case in three dimensions it is clear that five, but no more spheres, may touch one another (each touching all). If there be such things as atoms, and if they be spherical or of one curvature, not more than five can touch, each touching all. Chemical compounds are known containing more than five elements. But this circumstance does not obliterate the limit of the eutexia of alloys, which are neither atomic nor molecular.

#### *Salt Alloys.*

§ 207. It cannot be gainsaid that, vast as is the importance in the arts of the elementary metals and their alloys, yet in

terrestrial nature the interaction and relationship of compound bodies is at least of equal importance, and of far wider scope; for the science of such interaction and relationship constitutes the greater part of chemistry and petrology.

Amongst the non-metallic elements we should expect the class analogous with the eutectic alloys to be very restricted in number, on account of the chemical attitude of such elements towards one another, that is their tendency towards chemical union.

Chemical compounds, however, all of which may for brevity's sake be called salts, can give rise to an indefinite number of eutectic bodies; indeed to an indefinite number of series of such bodies. The whole of the preceding memoirs on Salt-solutions and Attached Water are in fact mainly a study of one such series. The cryohydrates are nothing else than eutectic alloys of the one salt called water with the various other salts. If instead of fused ice (water) we employ another fused salt, say fused table salt, we may expect to find it forming eutectic alloys with other salts, whose characteristic should be fusibility at a temperature lower than that of either (both) of its constituents.

§ 208. In choosing salts whose behaviour under such examination shall be as free as possible from ambiguity we must avoid:—

*First*, those which are decomposed when heated by themselves to anything like the temperature to which they are to be exposed in the experiment. And we are safe in this respect, if we confine ourselves to those which are not decomposed on fusion. For the bodies we are seeking should have temperatures of fusion below the temperature at which that one of its constituents fuses whose temperature of fusion is the lower of the two—it should be eutectic.

*Secondly*, must be avoided those which react on one another chemically, either in the sense of suffering double decomposition, or in that of direct combination whereby double salts are formed. It will be shown in § 225–227 that it is not always necessary to avoid the first of these contingencies. The possibility of double decomposition is of course avoided when the two salts used have either a common basic, or a common acid constituent.

*Thirdly*, are to be eschewed those salts which attack at high temperatures the vessels employed.

Amongst all salts perhaps Nitre answers these requirements best, as the body whose homologue is ice in the previous memoirs of Salt-solutions and Attached Water Nitrates do not form double salts with one another, nor with other salts (compare, however, Karsten). Nitre may be raised without suffering decomposition to a temperature far above its temperature of fusion ; possessing in this respect a wider range of available temperature than nitrate of ammonium, which might otherwise be preferable on account of its lower melting-point.

§ 209. In the following paragraphs, from § 210 to § 227, temperatures up to  $280^{\circ}$  C. were measured by means of a mercurial thermometer. Those above that range were determined by an air-thermometer with a horizontal stem about three feet long. The index was a plug of mercury. The total range was from about  $0^{\circ}$  to  $380^{\circ}$  C. As most of the experiments in which the air-thermometer was used were made on days on which the barometric pressure was nearly the same, no correction was needed. On other days the air-thermometer was standardized at the temperature of boiling water, with the mercurial one placed by its side in the water.

§ 210. *Nitre*.—I find that the temperature of fusion of pure nitre is  $320^{\circ}$  C.

§ 211. *Nitre and Chromate of Potassium*.—If nitre be fused in a large porcelain crucible and neutral chromate of potassium be added, some of the chromate is dissolved. The higher the temperature the larger the quantity. On suffering the solution to cool slowly, chromate of potassium separates out in fine powder, which sinks through the fused mass. The temperature falls till it reaches  $295^{\circ}$ , at which it remains constant ; and the liquid begins to solidify. The liquid portion is poured into a fresh crucible; and this may be repeated any number of times. The temperature of solidification is constant. The liquid being poured upon a cold slab solidifies to a mass, which has when cold precisely the colour of sulphur. Of this alloy 2.4881 grams gave 0.1226 chromate of barium. This corresponds to 0.0936 chromate of potassium, which is 3.76 per cent. Accordingly this alloy is:—

	Melting-point.
Nitre . . . . .	96.24
Chromate of potassium .	3.76

§ 212. *Nitre and Nitrate of Calcium.*—The three metals calcium, strontium, and barium promised to be of interest in furnishing nitrates alloyable with nitre. The method of experiment was precisely as before, the nitrates having been rendered anhydrous before they were added to the fused nitre. The bases were all separated and weighed as carbonates.

The eutectic alloy of nitre with nitrate of calcium has a melting-point of 251°. Of this, 1.8300 gram gave 0.2830 carbonate, or 0.4641 gram nitrate of calcium. This corresponds to 25.36 per cent.

§ 213. The eutectic alloy of nitre with nitrate of strontium has a melting-point of 258°. Of this, 1.9490 gram gave 0.3498 gram carbonate, or 0.5031 gram nitrate. This corresponds to 25.81 per cent.

§ 214. The eutectic alloy of nitre with nitrate of barium melts at 278°.5. Of this, 2.6100 grams gave 0.5860 gram carbonate, or 0.7773 gram nitrate of barium. This corresponds with 29.53 per cent.

Eutectic alloys of :-

	Melting-point.
Nitre . . . . .	74.64
Nitrate of calcium . . .	25.36
Nitre . . . . .	74.19
Nitrate of strontium . .	25.81
Nitre . . . . .	70.47
Nitrate of barium . . .	29.53

In this group strontium holds its accustomed intermediate place between calcium and barium ; but, both in regard to the melting-point and to the composition of its eutectic alloy, it more closely resembles the former than the latter.

§ 215. *Nitre and Nitrate of Lead.*—The eutectic alloy formed by these salts is of great interest, not only because the lead element, like the chromate of potassium and the nitrates of barium and strontium, cannot be fused alone without decomposition, but because it, the alloy, has a remarkably low melting-point, and because either constituent in excess of its quantity in the eutectic alloy raises the melting-point in a manner easy

to be followed. To the fused nitre the dry nitrate of lead is added, and on cooling one or other separates out in crystals easy to distinguish. More of the salt which is in fusion is added, until this is in its turn the one which separates on cooling. The same process having been repeated three or four times, the whole is allowed to lose heat as before. The temperature soon settles at 207° C., and thereupon the liquid begins to solidify as a beautiful white opaque porcelain-like mass, startlingly like the cryohydrates. The temperature may at first sink to 203° C.; and when in this condition of supersaturation, solidification is not to be induced by the introduction of dust of either of the nitrates, but begins when dust of the solid eutectic alloy is introduced. The temperature thereupon rises to 107°. This presumably proves that the alloy has a crystalline form of its own, different from those of its two constituents. Its composition was as follows, the lead being weighed as sulphate. The two specimens were from separate preparations, the only criterion of identity of composition being identity of melting-point.

(1) 2.8625 grams gave 1.2150 of sulphate of lead, or 1.3276 gram of nitrate of lead, or 46.38 per cent. of nitrate of lead.

(2) 2.3005 grams gave 0.9968 gram of sulphate of lead, or 1.0892 gram of nitrate of lead, or 47.34 per cent. Taking the mean, we have

Eutectic alloy of

	Melting-point.
Nitre . . . . .	53.14
Nitrate of lead . . . . .	46.86

§ 216. *Nitre and Sulphate of Potassium.*—Anhydrous neutral sulphate of potassium dissolves in fused nitre, and separates out therefrom as the fused mass cools in the form of a fine powder. It is advantageous to allow the mass to lose heat very slowly. As soon as the porcelain-like eutectic alloy begins to be formed, the liquid is transferred into a fresh crucible, and the solidification is continued. An alloy is thus finally obtained of the constant melting-point of 300°.

2.6625 grams gave 0.0836 gram sulphate of barium, corresponding to 0.0627 gram sulphate of potassium, or 2.36 per cent.

Eutectic alloy of	Melting-point.
Nitre . . . . .	97·64 { 300°.
Sulphate of potassium : .	2·36 }

§ 217. Putting together the results of §§ 211-214, we have the following table, in which the alloys are, like the cryohydrates of table § 88, arranged according to the lowness of the melting-points.

TABLE XLIII.

## Eutectic alloys with nitre.

Name of salt.	Temperature of fusion.	Per cent. of salt.	Per cent. of nitre.
Nitrate of lead .....	207°	46·86	53·14
Nitrate of calcium.....	251	25·36	74·64
Nitrate of strontium.....	258	25·81	74·19
Nitrate of barium .....	278	29·53	70·47
Chromate of potassium ..	295	3·76	96·24
Sulphate of potassium .....	300	2·36	97·64

Fused mixtures of nitre and the variable salt, which are richer in the salt than the eutectic alloy, give up that salt on losing heat ; those which are poorer give up nitre, until in both cases the eutectic alloy is reached. The eutectic alloy is the exact analogue of the cryohydrate ; and just as in the preceding memoir curves were drawn showing, on the one hand, the temperatures at which ice separates from salt-solutions of various strengths, weaker in salt than the cryohydrate, and, on the other, the temperature at which the salt, or occasionally a subcryohydrate, separates from such solutions as are stronger in salt than the cryohydrates, so, doubtless, the analogous curves could be drawn connecting the temperature at which solidification begins with the fused mixtures of salts (see § 223). And, again, as there are always two strengths of an aqueous solution, one stronger and the other weaker than the cryohydrate, which are both saturated at the same temperature below zero, one in respect to the salt and the other in respect to the ice, so with these fused mixtures there must be two such mixtures, from both of which a solid begins to separate at any given temperature between the melting-point of the most easily fused constituent and that of the eutectic alloy. § 223 is devoted to the tracing of this inquiry.

§ 218. The analogy is so perfect between the two groups of bodies (eutectic alloys and cryohydrates), that we may look with great confidence for homologous phenomena. The freezing mixture, or cryogen of my former memoirs, has its perfect counterpart amongst the salt-alloys, as follows :—

A layer of powdered nitrate of lead (46 parts by weight) is placed in the bottom of a wide test-tube. On this is laid a thin disk of mica, having a hole in the middle. A thermometer is fixed through the hole so that its bulb is half covered by the lead salt. Upon the mica, and so surrounding the top of the bulb, is piled some powdered nitre (54 parts). This tube is plunged into a bath of melted nitre, which is heated some few degrees above its melting-point, and until the thermometer registers about  $250^{\circ}$ . The thermometer is then used as a stirring-rod to mix the two salts. The mercury sinks to  $207^{\circ}$ , and remains pretty constant for a time at that temperature. The contents of the tube liquefy, and solid nitre is formed upon the outside of the tube. Now substitute ice for nitre, and perform the analogous experiment. The nitrate of lead and ice in the inner tube will form a freezing-mixture when stirred together, and this will cause ice to form on the outside, if the melted ice (water) in contact with it be not too warm.

§ 218A. Just as the eutectic metallic alloys had been nearly approached by Rudberg and others, so approximations to eutectic salt alloys have not been unknown. Thus M. Maumené (*Comptes Rendus*, 1883, xcvi. p. 1215) makes the very interesting statement that while neither nitrate of barium nor nitrate of lead can be fused *per se* without decomposition, they can both be so fused beneath a mass of nitrate of potassium or nitrate of sodium or a mixture of both. He states that an equivalent mixture of the nitrates of barium and sodium melts at about  $370^{\circ}$ ; and that when equal weights are taken, crystallization begins at  $322^{\circ}$ , and solidification takes place at  $288^{\circ}$ . Again, according to M. Maumené, equal weights of the nitrates of lead and sodium have a melting-point (*point fixe*) at  $282^{\circ}$  [we have seen that the eutectic alloy of these two fuses at  $268^{\circ}$  and contains 42.84 *per cent.* of nitrate of lead (see § 221)]. And again, M. Maumené, on taking equal weights of nitrate of sodium, nitrate of potas-

sium, and nitrate of lead, finds the melting-point  $259^{\circ}$ . [I find (§ 215) an eutectic alloy melting at  $186^{\circ}$  and containing 43.34 nitrate of lead.] It appears that none of the proportions given by M. Maumené are those of the eutectic alloys, and that accordingly the temperatures of solidification which he gives cannot be constant.

§ 219. *Eutectic Salt Alloys of Nitrate of Sodium.*—Nitrate of sodium fuses at  $305^{\circ}$ , and we might perhaps expect that its eutectic alloys would have lower fusing-points than the corresponding nitre alloys. The following experiments show that this is by no means the case.

§ 220. *Nitrate of Sodium with Nitre.*—Obtained by the method above described, the eutectic alloy of these two salts has the fusing-point of  $215^{\circ}$  C. Of this alloy 3.8885 grams were converted into neutral sulphates, having the joint weight 3.3135. This implies 2.5093 grams nitre and 1.3792 gram nitrate of sodium ; or

	Per cent.	Melting-point.
Nitrate of sodium . . . .	32.90	$215^{\circ}$ .
Nitrate of potassium . . . .	67.10	

For the specific gravity of this alloy, see § 228.

§ 221. *Nitrate of Sodium with Nitrate of Lead.*—This eutectic salt alloy has a melting-point of  $268^{\circ}$ . A weight of 3.3040 grams gave 1.2955 grams sulphate of lead, which corresponds to 1.4156 gram nitrate of lead.

	Per cent.	Melting-point.
Nitrate of sodium . . . .	57.16	$268^{\circ}$ .
Nitrate of lead . . . .	42.84	

§ 222. *A Tri-eutectic Alloy.*—Let us consider for a moment the alloy in § 219 to be a single salt, and find the eutectic alloy between this and nitrate of lead. The lowest melting-point is found to be  $186^{\circ}$ ; and the composition of the alloy, derived from the result that 2.9280 grams gave 1.1613 gram sulphate of lead or 1.2690 gram nitrate of lead, is as follows :—

	Per cent.	Melting-point.
{ Nitrate of potassium . . . .	38.02	$186^{\circ}$ .
{ Nitrate of sodium . . . .	18.64	
Nitrate of lead . . . .	43.34	

This of course implies that the above is the eutectic alloy of

these three salts. The eutexia of salt alloys of more than two salts is a very wide question upon which I can only here touch.

§ 223. The following experiment completes the analogy pointed out in § 218. Mixtures of nitre and nitrate of lead, both in the form of powder, were made in different ratios from 95 nitre and 5 of nitrate of lead, 90 of nitre and 10 of nitrate of lead, and so on ; these were put into test-tubes and heated in an oil-bath, which was kept continually stirred. The mixture was completely melted, and the temperature at which solidification began was observed. The observations, being repeated many times, gave the following results :—

Temperatures at which solidification begins in melted alloys of nitre with nitrate of lead of various strengths.

TABLE XLIV.

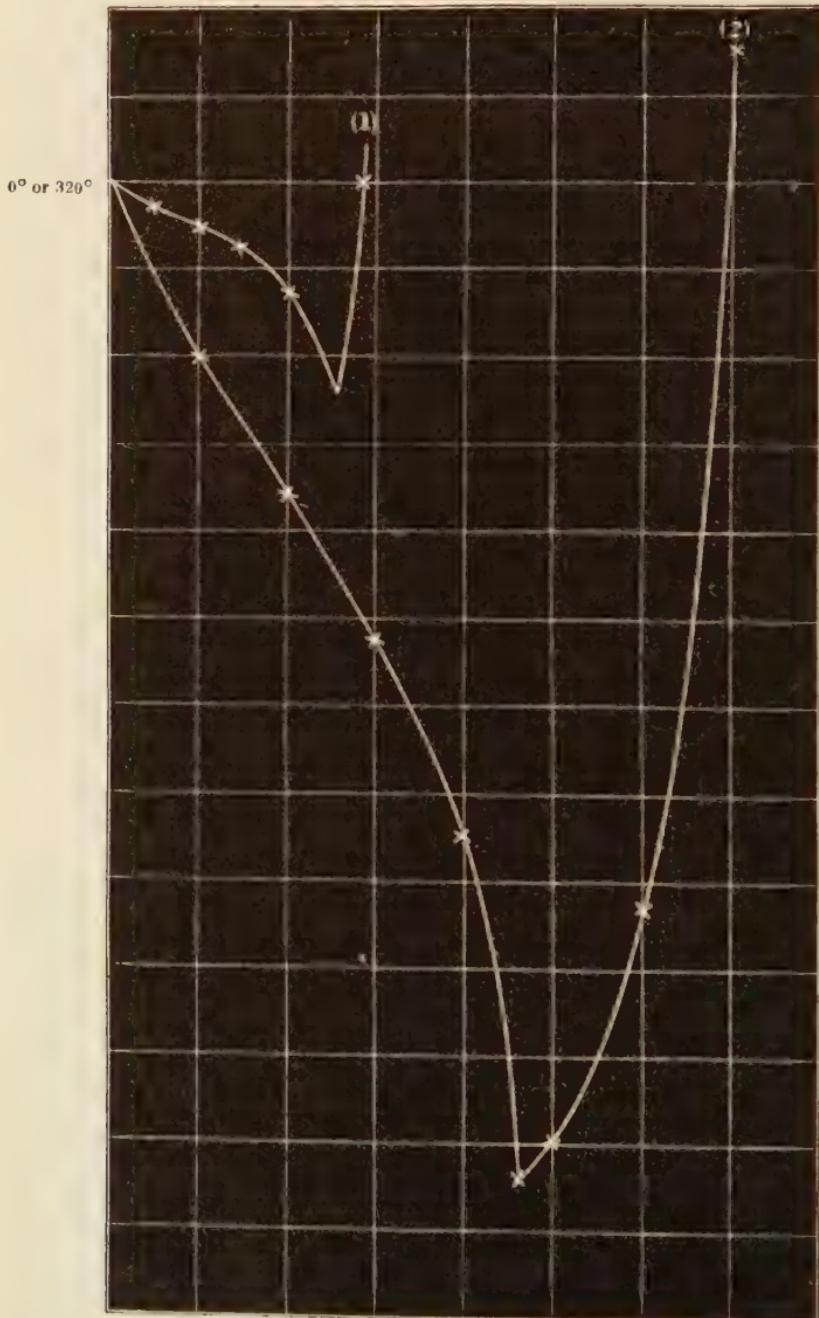
Nitre per cent.	Nitrate of lead per cent.	Temperature of beginning of solidifica- tion.	Nature of body separating.
100	0	320°	Nitre.
90	10	300	"
80	20	285	"
70	30	268	"
60	40	246	"
53·14	46·86	207	Eutectic alloy.
50	50	210	Nitrate of lead.
40	60	238	"
30	70	335 (?)	"

It is of course necessary to heat the mixed powders, in each case, beyond the temperature which proves to be the initial solidifying point of the mixed mass. On heating the column of powder it is noticed first to shrink and cake together to about a quarter of its former volume, reminding one of the baking of clays. Indeed all phenomena of so-called incipient fusion of compound bodies (the pasty state) may be due to what takes place here, namely the formation of an eutectic alloy.

The decomposition of both terms of this alloy, at temperatures not very much higher than 320°, puts a limit to the tracing of this curve further, but its general aspect is quite like that of the salt-solution (water) curves below zero, of which so many examples have been given in previous memoirs.

Mixtures consisting of 20 per cent. nitre and 80 per cent.

nitrate of lead, and even 10 per cent. nitre and 90 per cent. nitrate of lead, fuse together into clear liquids without decom-



position, but I have not determined the melting-points. At a higher temperature the red peroxide of nitrogen is evolved,

but I do not know whether it is or is not accompanied by oxygen.

In the figure curve (1) shows the solidification-temperatures of mixtures of nitrate of lead and fused ice (§ 152), and curve (2) shows the solidification-temperatures of mixtures of nitrate of lead and fused nitre. The abscissæ are on the same scale (1 millim. to 1 per cent. of lead salt). The ordinates are in (2) 1 millim. to  $1^{\circ}$  C. ; in curve (1) 1 millim. to  $0^{\circ}1$ . The curve (2) is fetched down so that the two have a common origin.

§ 224. One of the widest generalizations with regard to the behaviour of compound bodies towards one another is that which assumes, in the case of two salts, that the bases are shared in the first place by the acids, and that the result which often ensues, that one base and one acid are ultimately found in union to the exclusion of all others, is due to the successive withdrawal of such a combination when formed, either by its insolubility or volatility. Accordingly we must not be surprised that when the conditions of insolubility are varied, the final selection may be wholly changed. The salt alloy described in § 215, namely the eutectic alloy of nitre and nitrate of lead, when mixed with the eutectic alloy of nitre and sulphate of potash, § 216, and heated, forms a perfectly transparent liquid. Sulphate of lead, which is so insoluble in water, is soluble in fused nitre (see § 225) ; and a mixture may be got identical with that got on heating nitrate of lead with sulphate of potassium in the presence of nitrate of potassium. There is in both cases equilibrium between the bases and acids. When sulphate of lead is dissolved in fused nitre, it is to be noticed that, at a considerably increased temperature, the red oxide of nitrogen is given off, as when nitrate of lead is heated by itself. Both nitre and sulphate of lead, when heated by themselves, require a much higher temperature for their decomposition ; this seems to show the existence of nitrate of lead in the fused mixture. The liquidness of the fused alloy does not show that no sulphate of lead is present : a certain amount of lead is no doubt in union with sulphuric acid, but is soluble in nitre as other salts are soluble in water.

§ 225. *Nitre and Sulphate of Lead.*—On adding pure dry sulphate of lead to fused nitre, solution ensues the more

abundantly the hotter the liquid. The amount of sulphate of lead dissolved is, however, small, and the fusing-point is only lowered about  $5^{\circ}$ , standing now at about  $315^{\circ}$ . At temperatures above its melting-point, it would be unjustifiable to call such a liquid an alloy, because its composition, in all probability, depends upon its temperature in as far as that composition is referred to the distribution of acids and bases. As it cools it gives up sulphate of lead in little crystals which sink. At the temperature of  $315^{\circ}$  general solidification begins, and is completed.

Of this alloy 4.2725 grams were treated with water and a little alcohol, and the insoluble sulphate of lead was found to weigh 0.1968 gram, corresponding to 4.61 per cent.

Sulphate of lead requires for fusion *per se* a bright red, almost white heat. But it is thus found to dissolve in hot fused nitre, and it separates as such on cooling the fused liquid. For the geological value of this fact see § 230.

§ 226. *Sulphate of Calcium* behaves in a similar manner. Highly refractory by itself, it dissolves in fused nitre. The cooling mixture, after shedding the excess of sulphate above that required for the eutectic alloy, solidifies at a constant temperature of about  $315^{\circ}$ . The lime, separated as oxalate and weighed as carbonate, showed a percentage of sulphate of 0.93. For 3.4832 grams of alloy gave 0.0238 gram of carbonate, or 0.03237 gram of sulphate.

§ 227. *Nitre and Sulphate of Barium*.—Even the sulphate of barium, which is typical of aqueous insolubility, dissolves in fused nitre, depressing the solidifying point, however, almost inappreciably. A little separates on cooling, and 8.54 grams of the eutectic alloy, when boiled with water, gave 0.0852 gram of the insoluble sulphate, or 0.98 per cent. It may be noticed in passing that, as is well known to analysts, sulphate of barium is soluble to an appreciable extent in another fused nitrate, namely nitrate of hydrogen.

§ 228. *Specific Gravity of the Eutectic Alloy of Nitrate of Potassium and Nitrate of Sodium*.

Slabs of nitre, nitrate of sodium, and the eutectic alloy of the two were cast upon a surface of cold metal, the liquids themselves being when poured only a few degrees above their melting-points. Their specific gravities were found by

weighing them in oil of turpentine of ascertained specific gravity. I found the

Specific gravity of nitre.....	2.2028
"      "      nitrate of sodium .....	2.0469
"      "      the eutectic alloy .....	2.1328

If the two were to mix without either gain or loss of volume in the proportion found in § 220, namely 32.9 of nitrate of sodium and 67.1 of nitrate of potassium, the specific gravity of the alloy would be 2.149. The density found shows that there has been an expansion on the two associating themselves together to form the alloy. And this expansion is presumably in near connexion with the lowering of the melting-point.

§ 229. The generalization of Berthollet is only one aspect of the question of distribution. When a compound body  $a_x$  and another compound body  $b_y$  being brought together in watery solution give rise to an insoluble body  $a_y$  and a soluble one  $b_x$ , we have no more right to say that the change is brought about in virtue of the insolubility of  $a_y$  than that it is due to the solubility of  $b_x$ . Strictly speaking, it is due to the difference in solubility of the two. For the solubility of the one is as much concerned with the separation of the two new compounds as in the insolubility of the other. It is on this account that eutexia, without water, and as it exists in the case of two fused metals or anhydrous salts, may and must have a determining influence on the arrangement in ratio or kind of the constituents.

§ 230. *Geological and Mineralogical Significance of Eutexia.* — How the temperature of liquefaction of rocks may be lowered by the introduction of even small quantities of water will be discussed in my next memoir. It has been very diligently considered by Daubrée. Let us briefly examine the question of the interaction of rocks and their constituents, without, of necessity, the intervention of water.

In reviewing the analyses of Felspathic minerals, most of which, unless weathered after solidification, appear to be essentially anhydrous, we find them to be silicates of potassium and aluminum, in which, to use the common expression, the potassium is partly replaced by sodium, calcium, magnesium, and manganese, the aluminum by iron. That water is not

essential to the formation of this kind of mineral, is proved by the occurrence of it in copper and iron furnaces. Mica, on the other hand, appears always to contain water, sometimes as much as three or four per cent., with a lesser percentage of silica than felspar ; it contains generally a far larger proportion of aluminum and of iron ; the abundance of the latter element may indeed be considered, together with its deficiency in silica, as its distinguishing characteristic, chemically speaking, from orthoclase.

Silica—the great earth-acid, a title which it shares with carbonic acid, whose other realm is the air, and to some extent with hydrochloric acid, whose proper region is the sea—appears both in the anhydrous form and with as much as eleven per cent. of water. By its union with alumina it gives rise to clay, slate, and the minerals staurolite, andalusite, kyanite ; with lime to Wollastonite ; with magnesia (and iron) to bronzite ; with lime and magnesia (and iron) to augite and diallage ; with magnesia and iron (and lime) to hypersthene and olivine ; with magnesia, lime, and iron to hornblende ; with iron to Fayalite, and so on.

If, now, we adopt the often-asserted theory that variations in minerals belonging to the same class are brought about by the exchange of more or less of one base by another, the analyses land us in a difficulty, which seems insuperable. Let us suppose, for instance, that we have pure Wollastonite, consisting of

Silica	51.73,
Lime.	48.27.

Replacing part of the lime by magnesia and iron, say 23.51 by 18.55 magnesia and 0.99 protoxide of iron, the silica rises to 55.15, and gives us an excellent example of augite (neglecting the manganese and alumina of that body).

	V. Bonsdorff.
Silica	54.83
Lime	24.76
Magnesia	18.55
Protoxide of iron	0.99
Protoxide of manganese	0.32
Alumina	0.28

But next let us examine hornblende, an analysis of which by V. Bonsdorff is given.

Silica . . . . .	60.10
Magnesia . . . . .	24.31
Lime . . . . .	12.73
Protoxide of iron . . . .	1.00
Protoxide of manganese	0.47
Alumina . . . . .	0.42
Hydrofluoric acid . . .	.83
Water . . . . .	.15
	—
	100.01

These bases, neglecting the water and hydrofluoric acid, require together 51.83 of silicic acid, instead of 60. No process of exchange of one base for another can make hornblende out of Wollastonite. It is essentially acid, unless in those varieties of amphibole which contain a considerable proportion of alumina; these, indeed, may be basic, acid, or neutral, according as the alumina is considered as a base saturating the silica, or an acid saturating lime or magnesia, or partly in the one predicament and partly in the other. As Wollastonite occurs along with amphibole and augite, there does not appear sufficient ground for this essential difference on the replacement theory.

I submit that, according to analogy, we should regard compound rocks and minerals, other than sedimentary rocks, as representing various kinds of eutectic alloys. We may for the sake of argument start from some known definite rock which is a true chemical compound, such as orthoclase, and trace the probable reactions between this and other rocks; or we may take a rock, like granite or syenite, of indefinite composition, and examine the probable assortment of its constituents on cooling. Starting with the melted mass, my experiments with salts have, I maintain, established that the clear molten granite will in cooling throw off as solids atomically definite salts, the last alloy to remain liquid being the eutectic alloy, which is constant only in composition in the sense in which such a body is so. It would follow therefore that the micas are the eutectic alloys of the proximate elements, or salts of

the melted granite. Quartz and felspar being both molecularly constituted, undergo solidification before mica. On account of the enormous effect which even a little water has in reducing the melting-point \* and because silica is soluble in water, it is probable that the order of solidification is first felspar, and then quartz, and lastly mica. Quartz is thus speaking *en gros* pseudomorphic to felspar, and mica to both ; all three are sometimes in this mass-sense pseudomorphic to slate, and mica is especially so. If fused nitre be saturated with nitrate of lead and sulphate of potash, and gradually cooled, sulphate of lead first separates, then sulphate of potash with sulphate of lead, then the eutectic alloy of all three. The sulphate of lead represents the felspar, the sulphate of potash with sulphate of lead represents the quartz, and the eutectic alloy represents the mica (see also § 38, *Phys. Soc. Proc.* 1874). Tourmaline and hornblende are probably both eutectic, whilst olivine is probably not.

§ 231. As to the great rock-masses themselves, if we assume that the earth is a drop of fused rock alloy with a solid crust, and that its history had been one of gradual undisturbed and symmetrical cooling, it is clear that, apart from sedimentary formations, the oldest solid rocks are those formed nearest the surface. But the disturbing causes are manifold: the earth-crust is under stress on account of the loss of volume on cooling. This strain is unequally distributed, on account of the want of sphericity of the earth's form, and on account of the centrifugal pressure towards the equator. Extra-terrestrial influences, such as the conjunction and apposition of the sun and moon and the variation in solar radiation, are asymmetrical, so that the earth's crust heaves and cracks and allows the eutectic melted alloy to break through, and as an intrusive mass metamorphose and overlie the older formations. Once rendered asymmetrical, the geographical features give rise to climates and weathers, and determine the formation of the sedimentary strata.

\* See Daubrée, *Géologie expérimentale*. Also my next memoir, §§ 339-345.

**XII. On a "Speed Indicator" for Ships' Propellers. By Sir ARCHIBALD CAMPBELL of Blythswood and W. T. GOOLDEN\*.**

[Plate IX.]

IN February of last year, when visiting one of H.M. Dockyards, it was pointed out to us that a very urgent need was felt of some means of indicating with certainty the speed of naval engines, especially in ships carrying twin-screws, where the engines are not only distinct, but separated from each other by iron bulk-heads which prevent any communication between the two engine-rooms. The authorities intimated also that it was desired that several indications should be made simultaneously in various parts of the ship, and that the apparatus should be as far as possible automatic, and require no trouble or attention.

There are at present one or two instruments in existence for this purpose, but their indications are found to be untrustworthy when at sea ; and we were warned that no instrument in which the force of gravitation played a part would be likely to receive any attention at the Admiralty. This consideration excludes the use of ball-governors or of any device depending on the weight of a fluid column ; and led us to consider whether the desired conditions could not be fulfilled by a purely mechanical arrangement founded on the ordinary equation involving angular velocity,

$$v = r\omega.$$

It was at first difficult to see how this principle could be applied to a direct measure of  $\omega$ , as no simple means are known whereby the variation in the velocity  $v$  of a point moving in a straight or curved path can be continuously measured. But it was soon apparent that the variable angular velocity  $\omega$  of a body A can be compared with the constant angular velocity  $\omega'$  of another body B, if a point on B at a distance  $r'$  from its axis of rotation has the same linear velocity as a point on the circumference of A. We then get

$$\omega = \frac{\omega'}{r'} r,$$

in which  $\frac{\omega'}{r'}$  is constant, and thus  $\omega$  varies as  $r'$ .

\* Read May 24, 1884.

The condition is evidently satisfied by a disk pressing on the surface of a cone revolving at a uniform speed ; for the linear velocity of the point in the perimeter of the disk which is in contact with the cone, being identical with that of the corresponding point of the cone, will be proportional to the radius of the corresponding circular section of the cone, and consequently to the distance of the point of contact from the apex of the cone. If, further, the disk forms the nut of a screw rotating in the opposite direction to the cone, and the axis of the screw is placed parallel to the side of the cone, it is obvious that the nut and screw must have the same angular velocity for the nut to be at rest on the screw ; and the disk will therefore take up a different position on the screw as the velocity of the latter changes in value.

In the "Blythswood Speed Indicator" the screw is driven by the engine or shaft whose speed is to be indicated, while the cone has a constant speed communicated to it by clock-work. A scale placed under the screw shows the speed of the nut and screw when the nut is at rest ; and by a series of electric contact-pieces attached to a cable, the indications can be transferred to dials placed at any distance from the machine.

When the engines reverse, a clutch keeps the screw revolving always in the same direction, and at the same time pulls over a commutator placed in the electric circuit, so that the dials show not only the speed, but also the direction of motion, ahead or astern.

The clock is wound by the engine, and stops when the machinery is at rest ; and having a carefully balanced friction-governor, it is independent of gravity, and therefore keeps its time under all conditions of wind and weather.

We propose to add to the instrument a drum carrying prepared paper, upon which as it revolves a pencil will continuously trace the position of the nut, and thus keep a record of the performance of the engine for future reference.

The same principle can evidently be applied to a comparison of the speeds of two engines or rotating shafts, where both are variable, if one drives the cone and the other the screw, for  $\frac{\omega}{\omega'} = \frac{r'}{r}$ , in which  $r$  is constant.

We desire in conclusion to express the obligation we are under to Mr. Hilger for the admirable skill and patient intelligence with which he has successfully carried out our idea.

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**XIII. *The Gas-Engine Indicator-Diagram.* By Professors  
W. E. AYRTON, F.R.S., and JOHN PERRY, M.E.\***

[Plate X.]

THE members of this Society are probably aware that gas-engines are now largely in use, and that their use is still extending rapidly. There can be no doubt that gas-engines would be largely used, even if they were wasteful of fuel, on account of their being always ready to start or stop, and their requiring so little attention ; but it is gradually becoming clearer that even small specimens of this kind of engine, whose history is merely beginning, are in actual fact less wasteful of fuel than the largest and most carefully constructed steam-engines. It is, for example, a demonstrated fact that, with a Dowson's generator not larger than the boiler used in the corresponding steam-engine, an Otto engine uses only 1.1 lb. of coal per indicated horse-power per hour. It is therefore not unreasonable to suppose that gas-engines will soon be employed even in the propulsion of ships.

The rapid growth of this new application of science renders it necessary that help should be given to practical men to enable them to use such observations as they are constantly making. This paper is intended to teach such men a *method* of obtaining information from the indicator-diagram of a gas-engine.

**2. *The Action in the Otto Gas-Engine.***—This large model which we exhibit has been constructed in the workshop of the Finsbury College, to enable students to follow the motions of different parts of the gas-engine. It will be seen that when the piston is at the end of its stroke, only what we call the clearance-space behind it is filled with fluid. This fluid is a mixture of carbonic acid, water-vapour, and nitrogen, whose

\* Read April 26, 1884.

temperature is about  $410^{\circ}$  C.\* if there was an immediately previous explosion. The temperature of the clearance-space fluid may be anything between  $410^{\circ}$  C. and the temperature of the atmosphere, depending on how recently an explosion has taken place. As the piston moves forward it draws into the space a mixture of gas and air. At the end of the forward stroke the pressure of the mixed fluid is nearly that of the atmosphere; in the back stroke the fluid is compressed. At the beginning of the next forward stroke the fluid is ignited, and rapid development of heat results, causing great increase in pressure, the pressure gradually diminishing until, just before the end of the forward stroke, the fluid is allowed to escape. In the next back stroke the piston drives the fluid out of the cylinder with the exception of what remains in the clearance, and thus completes a cycle of operations. In fig. 1 (Pl. X.) indicator-diagrams show the nature of the alterations in pressure and volume going on during the compression and working parts of the cycle; distances measured from O L representing pressure in pounds per square inch from vacuum, and distances measured from O P representing volume of the fluid, the unit of volume being the volume described by the piston moving through one foot of the length of the cylinder.

Four different diagrams are given whose compression parts practically coincide, the differences in their ignition parts being due to differences in the amounts of gas supplied. We have not thought it necessary to give a complete diagram in which the dismissal and suction parts of the cycle should be represented.

The shape of the diagram is materially modified by the recentness of the last explosion, as this affects the temperature of the fluid before compression, and so modifies the actual amount of the mixture of gas and air entering the cylinder. To a less degree the shape of the diagram is affected in the discharge part of the cycle by the recentness of an explosion,

\* In our own observations at Finsbury we have not used any specially contrived apparatus, as our investigations were really for the purpose of enabling students to illustrate for themselves a course of lectures delivered by one of us on the Gas-engine. Hence we have taken the temperature of  $410^{\circ}$  C. as the exhaust temperature, instead of  $300^{\circ}$  C. given by our own measurements with the Siemens pyrometer. A correction of this temperature would perhaps lessen the number  $1.57$  W and increase  $0.37$  W, given in § 9.

as a recent explosion will have given the exhaust passages a higher temperature.

3. *The Nature of the Working Fluid.*—For the purpose of showing the nature of the working fluid we have constructed Table I. It will be seen from this that a mixture of 6.760 cubic feet of air and coal-gas becomes, after complete combustion, 6.4977 cubic feet of carbonic acid, water-vapour, and nitrogen, reduced to the same pressure and temperature without condensation of the water-vapour. Now as there is always an excess of air, and as the mixture before combustion has added to it nearly six cubic feet of the products of previous combustions, we have something like 13.3 cubic feet before combustion becoming 13.0377 cubic feet after combustion, at equivalent pressures and temperatures. The contraction is only about 2 per cent. We therefore conclude that we may regard the fluid in a gas-engine as a fluid which, however it may receive heat, obeys approximately the characteristic law,

$$\frac{pv}{T} \text{ constant}$$

(where  $p$  is pressure,  $v$  volume, and  $T$  the absolute temperature), in so far as mechanical actions are concerned. That is, we may speak of it as a perfect gas, which receives heat from without, neglecting the fact that it is its own molecular energy which appears as heat. It is also approximately true that the ratio of the specific heats of the fluid is unchanged by combustion taking place.

In Table II. we give a similar comparison for Dowson gas :—

2.1325 cubic feet of combustible mixture become 1.9143 cubic feet ;

or, taking into account the clearance-space and its products of past combustions, we have, say,

4 cubic feet becoming 3.7818 cubic feet ;

or contracting by nearly  $5\frac{1}{2}$  per cent. of its volume.

In Tables III. and IV. we calculate the specific heat of a mixture of 1 cubic foot of coal-gas, 5.76 cubic feet of air, and 4.5 cubic feet of products of a previous combustion, before and after combustion takes place. The Centigrade scale of temperature is employed.

In Tables V. and VI. similar calculations are made for the usual mixture of Dowson gas with air and products of previous combustion.

TABLE I.—Coal-Gas.

Hydrogen, H <sub>2</sub> .	Carbonic oxide, CO.	Marsh- gas, CH <sub>4</sub> .	Olefiant gas, C <sub>2</sub> H <sub>4</sub> .	Tetrylene, C <sub>4</sub> H <sub>8</sub> .	Nitrogen, N.	Carbonic acid, CO <sub>2</sub> .	Water- vapour. H <sub>2</sub> O.	Total.
0·4600	0·0750	0·3950	0·0253	0·0127	0·0050	0	0·0200	
191·12	190·02	592·6	932	1702	0	0	0	
87·92	14·25	234·1	23·58	21·61	0	0	0	381·46 or 530,230 foot pounds.
0·5	0·5	2	3	6	0	0	0	
1·0	1·0	3	4	8	0	0	0	
0·2300	0·0375	0·780	0·0759	0·0762	0	0	0	1·2096 cub. ft. of oxygen per cub.
0·460	0·075	1·1850	0·1012	0·1016	0·005	0	0·020	or 5·760 " " air " " " or 1·9478 + 4·5499 of nitrogen, or 6·4977.

TABLE II.—Dowson Gas.

Hydrogen, H <sub>2</sub> .	Carbonic oxide, CO.	Marsh- gas, CH <sub>4</sub> .	Olefiant gas, C <sub>2</sub> H <sub>4</sub> .	Tetrylene, C <sub>4</sub> H <sub>8</sub> .	Noncom- bustible.	Total.
0·1873	0·2507	0·0031	0·0020	0·0011	0·5555	
191·12	190·02	592·6	932·05	1702	0	88·99, or 123696·1 foot-pounds.
35·79	47·63	1·837	1·864	1·872	0	
0·0936	0·1254	0·0062	0·0060	0·0066	0	0·2378 cub. ft. of oxygen per cub. ft. of gas, or 1·1325 " air " " " or 4·641 + 4·898 of N in gas + 0·657 of CO <sub>2</sub> in gas
0·1873	0·2507	0·0093	0·0080	0·0088	0	+ 8947 of N in air introduced = 1·9143.

TABLE III.—Coal-Gas before Combustion.

Constituent.	Amount in fluid.	Specific heat at constant pressure per unit volume.	Specific heat at constant volume per unit volume.		
	Cubic feet. $q.$	$C_p.$	$C_v.$	$qC_p.$	$qC_v.$
Hydrogen .....	0.46	.2359	.99 $\times$ 168	.1085	.4554 $\times$ 168
Carbon monoxide	0.075	.237	1 "	.0178	.0750 "
Marsh-gas .....	0.3950	.3277	1.54 "	.1294	.6082 "
Olefiant gas .....	0.0380	.4106	2.03 "	.0156	.0771 "
Nitrogen .....	0.0050	.237	1 "	.0012	.0050 "
Water-vapour .....	0.0200	.2984	1.36 "	.0060	.0272 "
Air .....	5.76	.2374	1 "	1.3680	5.760 "
Products .....	4.5	.2581	1.124 "	1.1614	5.058 "
Total .....	11.253	.....	.....	2.8079	12.066 $\times$ 168 or 2.027
Or $C_p = 0.2496$ , $C_v = 0.1802$ . Ratio ..... 1.385.					

TABLE IV.—Coal-Gas after Combustion.

	Cubic feet. $q.$	$C_p.$	$C_v.$	$qC_p.$	$qC_v.$
Water-vapour ...	1.3714	.2984	1.36 $\times$ 168	.4092	1.865 $\times$ 168
Carbon dioxide ...	0.5714	.3307	1.55 "	.1889	.8855 "
Nitrogen .....	4.5554	.2370	1 "	1.0790	4.5554 "
Total .....	.....	.....	.....	1.6771	7.3059 $\times$ 168 or 1.227
Or $C_p = 0.2581$ , $C_v = 0.1889$ . Ratio ..... 1.367.					

TABLE V.—Dowson Gas before Combustion.

	Cubic feet. $q.$	$C_p.$	$C_v.$	$qC_p.$	$qC_v.$
Hydrogen .....	.1873	.2359	.99 $\times$ 168	.0442	.1854 $\times$ 168
Carbon monoxide.	.2507	.237	1 "	.0594	.2507 "
Marsh-gas .....	.0031	.3277	1.54 "	.0010	.0048 "
Olefiant gas .....	.0031	.4106	2.03 "	.0013	.0063 "
Nitrogen .....	.4898	.237	1 "	.1161	.4898 "
Carbon dioxide ...	.0657	.3307	1.55 "	.0217	.1018 "
Air .....	1.1325	.2374	1 "	.2689	1.1325 "
Products .....	2	.2594	1.1323 "	.5188	2.2646 "
Total .....	4.1322	.....	.....	1.0314	4.4359 $\times$ 168
				.2496	1.0735 $\times$ 168 or 1.803
Ratio ..... 1.385.					

TABLE VI.—Dowson Gas after Combustion.

	$q$ .	$C_p$ .	$C_v$ .	$qC_p$ .	$qC_v$ .
Water-vapour ...	0.2019	.2984	$1.36 \times 168$	.0602	$.2746 \times 168$
Carbon dioxide ...	0.3279	.3307	1.55 "	.1084	.5083 "
Nitrogen .....	1.3845	.2370	1 "	.3281	1.3845 "
Total .....	1.9143	.....	.....	.2594	$1.1323 \times 168$ or .1902
Ratio ..... 1.3637.					

The specific heats here given are those of the constituents in the cold state. Seeing, however, that there is no great change due to combustion, we may for many practical purposes assume that the specific heats remain the same at all temperatures. We have less right when using Dowson gas than when using coal-gas to make our assumption, which is that the fluid in the gas-engine, from the beginning of its compression until it is allowed to escape, behaves like a perfect gas, receiving heat from an outside source.

4. *Study of the Shapes of the Compression and Expansion parts of the Diagram.*—The first problem which comes before us is the determination of the shape of the indicator-diagram. For the sake of illustration we mean to investigate the series of diagrams shown in fig. 1, diagrams taken from a 6-horse power Otto engine at the Finsbury College, using coal-gas. It will be observed that, although the ignition parts of the various diagrams differ greatly, on account of differences in the amounts of gas supplied, the curves agree in their compression and expansion parts. It is known to us that the clearance-space is 0.4 of the whole space occupied by fluid when the piston is fully at the end of its stroke. If  $\lambda$  is the distance in feet passed through by the piston from the end of its stroke, the stroke being  $1\frac{1}{2}$  foot, the clearance is 0.889 foot, and  $\lambda + 0.889$ , or  $l$  feet expresses the volume of the fluid at any instant. Measurements of  $l$  and  $p$  were made on the expansion-curves of the indicator-diagrams, and tabulated with  $\log l$  and  $\log p$ .

We are making arrangements for measuring the clearance-space with accuracy. The above assumption is made from

statements of the manufacturers, and may possibly be slightly in error. Such an error is of but small importance to us at present, as our object is to teach a method of study rather than to give results of the use of the method.

If we assume the law of the expansion-curve to be

$$pl^m \text{ constant},$$

we have  $\log p + m \log l = k$ ; so that when we plot  $\log p$  and  $\log l$  on squared paper as coordinates of points, these points ought to lie in a straight line if our assumption is correct. Fig. 2 (Pl. X.) shows how the points determined by the measured numbers lie; and it is obvious that they lie very nearly in a straight line. Taking the straight line which lies most evenly among them, we find that it is defined by

$$\log l = 0.313, \text{ when } \log p = 1.7,$$

$$\log l = 0.0425, \text{ when } \log p = 2.1.$$

Hence

$$1.7 + 0.313 m = k,$$

$$2.1 + 0.0425 m = k.$$

Hence

$$m = 1.479 \text{ and } k = 2.1629.$$

Now

$$\log 145.5 = 2.1629.$$

Hence the law of expansion is

$$pl^{1.479} = 145.5. \quad \dots \dots \dots \quad (1)$$

In the same way we find that the law of the compression-curve is

$$pl^{1.304} = 39.36. \quad \dots \dots \dots \quad (2)$$

It is obvious that the expansion-curve (1) is steeper than the adiabatic, if we assume that the ratio of specific heats of the fluid is 1.37, as the equation of the adiabatic curve is

$$pl^{1.37} = \text{constant.}$$

Again, the compression-curve (2) has less slope than the adiabatic.

5. *Influence of Vibrations of the Indicator-spring.*—We wish to point out that it is exceedingly necessary, in obtaining the law of expansion, to take many points in the curve, and, either

by using the algebraic method or by the use of squared paper, to determine the most probable values of the constants. Engineers are constantly in the habit of determining these constants from measurements of the coordinates of two points only in the curve, forgetting that the position of either point may be much influenced by the vibrations of the spring of the indicator. The sinuous shape of the expansion-curve is specially noticeable in the early part of the expansion-curves of gas-engine diagrams.

It is further to be remarked that the vibration of the indicator-spring is very visible in the expansion part, because we have every reason to believe that the expansion part ought to have no sinuosities ; but it is our belief that this vibration has its effect on the explosion part of the curve as well, and that it is of the utmost importance to find some means of eliminating the effects produced by these vibrations of the indicator-spring.

In our communication to the Journal of the Society of Telegraph Engineers, p. 391, vol. v. (1876), we showed how to eliminate such vibrations in any case where the effect to be measured followed a regular law of increase or diminution, as in the case of the expansion part of this indicator-diagram. We have not yet sufficient information to enable us to employ this method on the explosion part.

The rule which we arrived at is as follows:—Draw two curves, A and B, through the highest and lowest points of the wavy curve which represents the actual observations : draw ordinates : the points of bisection of the parts of the ordinates intercepted between A and B lie on the correct curve.

6. *Empirical Formula for the whole Diagram.*—Now, inasmuch as the compression and expansion parts of all the curves follow the same laws, it would seem to be important to obtain one general formula for all the diagrams with one or more variable parameters. We have found that when we produce the expansion-curve (using formula 1), as shown at B M (fig. 1), and when we divide the pressure Q R at any part of the stroke by the corresponding ordinate L R of the expansion-curve, doing this for many parts of the stroke, we get the ordinate of an interesting curve. We have done this for the four diagrams of fig. 1, and obtain the four curves A Q B D, A E C D,

A F D, A G H of fig. 3. From a study of these curves, which are nearly formed of straight lines, it will be found that the ignition and expansion parts of any diagram satisfy approximately the law

$$p = 145.5 l^{-1.479} \{ \kappa' + n\lambda - \sqrt{(\kappa - n\lambda)^2 + s} \}. \quad \dots \quad (3)$$

The smaller the value of  $s$  the more nearly do the curves of fig. 3 approach straight lines. In our present case  $\lambda = l - 0.889$ ,  $\kappa' = 0.6343$ ,  $\kappa = 0.3637$ ;  $s = 0.0087$ , and  $n$  has different values for the four diagrams. These constants are evidently easily calculated from any diagrams. For the curve shown as A B C D in fig. 1 (Pl. X.) the value of  $n$  is 2.2876. Using this value and calculating  $p$  for the following values of  $l$ , we have

TABLE VII.

$\lambda$ .	$l$ .	Observed. $p$ .	Calculated. $p$ .	Expansion- curve calculated. $p$ .
0	.889	45	45	173
.061	.950	86	83	157
.111	1.000	108	108	146
.170	1.059	123	124	134
.211	1.100	126	125	126
.311	1.200	111	111	111
.511	1.400	88	88	89
.711	1.600	72	73	73
.911	1.800	60	61	61
1.111	2.000	52	52	52

The differences between the observed and calculated values of  $p$  are within the limits of errors of observation therefore. It may be that there is a discontinuity in the ignition-curve at  $\lambda = .061$  for a mixture of gas and air; but no discontinuity shows itself in the indicator-diagram in a sufficiently marked manner to be distinguished from vibrations due to the spring of the indicator.

As we have already stated, the recentness of the last explosion affects the temperature of the mixture of gas and air, and therefore the mass of the mixture. Hence we often find that the expansion parts of successive indicator-diagrams do

not coincide. The law

$$p = Ml^{-1.479} \{ \kappa' + n\lambda - \sqrt{(\kappa - n\lambda)^2 + s} \},$$

where  $\kappa'$ ,  $\kappa$ , and  $n$  are constants, satisfies all the diagrams.

$n$  is a constant whose value depends on the point in the stroke at which the maximum pressure occurs; and this, for a given speed of engine, depends principally on the proportion of gas to air in the mixture;

$M$  is a constant which depends on the recentness of the last explosion.

7. *Simple Formulae for the Ignition and Expansion parts of the Diagram.*—The complete formula (3) assumes no want of continuity in proceeding from the ignition to the expansion part of the diagram. For the sake of ease in practical calculations we may, however, assume that the ignition- and expansion-curves are quite discontinuous, employing some method of indicating continuity when results are plotted on squared paper. In this case we assume that the lines of fig. 3 are quite straight, so that

$$\text{the ignition part of curve is } (a + b\lambda)\kappa l^{-m}, \dots \quad (4)$$

$$\text{the expansion part of curve is } \kappa l^{-m}. \dots \quad (5)$$

In our diagrams,

$$\kappa = 145.5, \quad m = 1.479;$$

Also  $a = 0.257$ .

In curve A B C D,  $b = 4.372$ ;

“ A E D,  $b = 1.457$ ;

“ A F D,  $b = 0.782$ ;

“ A G H,  $b = 0.313$ .

To use formula (4) in any given case. Find by the method already given in § 4 the constants of equation (5) to the expansion part. Assume that the ignition is complete when  $\lambda = \lambda_1$ . Let the pressure at the beginning of the stroke be  $p_0$ ; calculate the value of  $\kappa l^{-m}$  when  $\lambda = 0$ , that is, when  $l$  = clearance or  $l_0$ , say; then

$$p_0 \div \kappa l_0^{-m} \text{ is } a,$$

and  $a + b\lambda_1 = 1$ ;

so that

$$b = \frac{1-a}{\lambda_1},$$

or  $a = \frac{p_0}{\kappa} l_0^m$  and  $b = \frac{1 - \frac{p_0}{\kappa} l_0^m}{\lambda_1}$ .

8. *The Rate at which the Fluid receives Heat as calculated from its Volume and Pressure.*—We shall now proceed to calculate the heat received by the fluid. This we shall do as if, instead of there being combustion going on among the particles of the fluid, we had the fluid a perfect gas receiving heat from a great number of little furnaces, or pieces of hot wire immersed in the fluid. Besides the heat here considered we have the heat radiated to the cold cylinder.

If  $A$  is the area of the piston in square inches,  $p$  the pressure of the fluid in pounds per square inch, and  $l$  the distance moved through by piston in feet, the work done by the fluid on the piston in an element of length  $dl$  is

$$Ap dl \text{ foot-pounds.}$$

It is evident that if we represent the heat which is received by the fluid in the length  $dl$  by

$$Aq dl \text{ foot-pounds,}$$

we may regard  $q$  as the rate (per foot-travel of the piston) at which heat is received by the fluid, just in the same sense as  $p$  the pressure is the rate at which work is done by the fluid; and a comparison of  $q$  and  $p$  shows at once the comparison between the rates at which heat is being received and work is being done.

Now, since we consider the fluid to behave like a perfect gas, we know from thermodynamics that

$$q = \frac{1}{\gamma-1} \left( \gamma p + l \frac{dp}{dl} \right), \quad \dots \quad (6)$$

where  $\gamma = 1.37$  (see §§ 3 and 4); and it is obvious that the relation of  $p$  to  $q$  is not altered in any way by altering the scale to which  $l$  or  $p$  is represented in the indicator-diagram.

We have taken three methods of drawing the curve whose ordinate is  $q$ . In the first method a list of the values of  $p$  was made out from careful measurements of the curve A B C D (fig. 1), for values of  $l$ , 0.889, 0.9, 0.911, 0.922, 0.933, 0.944, &c. The observed increment of  $p$  divided by the increment of  $l$  was taken to represent the value of  $\frac{dp}{dl}$  for the mean value of  $l$ . In this laborious way  $q$  was obtained for many values of  $l$ , and the curve E F G H (fig. 4) repre-

sents our result. It is obvious that the rate at which the fluid receives heat is greatest at the very beginning of the stroke, falling off during the ignition period, much more rapidly at the end of the ignition period ; and in G H we see that the fluid is losing heat during what we call the expansion part of the stroke. In the same figure the actual indicator-diagram is shown in A B C D, the pressure being shown to the same scale as the ordinate of the heat-diagram.

The area between E F G H, the line O $\lambda$ , and any two ordinates, shows in foot-pounds the heat given to the fluid between the two positions, to the same scale as that to which the area of the indicator-diagram represents work done.

Another method which we have taken is this. To find  $q$  corresponding to a point S (fig. 5) on the indicator-curve. Draw a tangent S R to the indicator-curve, meeting the line O P in R. O P and O L are the lines O P and O L of fig. 1. Draw from R a line R Q parallel to O L, meeting the ordinate from S in the point Q. Then the distance S Q, or rather T S - T Q, represents

$$l \frac{dp}{dl}.$$

Measuring S Q, therefore, paying attention to the fact that it may be negative or positive, adding to it  $\gamma$  times S T and dividing by  $\gamma - 1$ , we obtain the ordinate  $q$  of the heat-curve.

Another method is to calculate  $q$  as given in (6), by actual differentiation of  $p$  as given in (3). We have employed this method, and believe that our result, in which the early part of the curve E F (fig. 4) is less steep than there shown, is probably more nearly true than what is given in fig. 4. We do not put our result forward at present because there may be a discontinuity in the explosion part of the curve, as Table VII. shows that at  $\lambda = 0.061$  the empirical formula does not give the observed pressure; and until we know how to eliminate vibrational effects of the indicator-spring, we have preferred only to publish the curve E F G H which has been obtained from the actual diagram, the expansion part only having been corrected for vibrations. As we know that the expansion part follows a law

$$p = \kappa l^{-m},$$

it is obvious that

$$q = \frac{\gamma - m}{\gamma - 1} p,$$

being proportional to the pressure. Now, comparing this result with the part G H (fig. 4), we see that G H is not quite correct, although determined from most careful measurements of the indicator-diagram. We see here an illustration of the great importance of obtaining a formula such as that given in (3) for the shape of the indicator-diagram.

9. *Total Heat and Work of One Cycle.*—The integral of  $q \cdot dl$  multiplied by the area A of the piston in square inches gives the total heat received by the fluid during any part of the stroke, and is evidently

$$A \int_{l_1}^{l_2} q \cdot dl = \frac{A}{\gamma - 1} (p_2 l_2 - p_1 l_1) + A \int_{l_1}^{l_2} p \cdot dl.$$

Taking from the diagram

$$p_1 = 44.5, \quad l_1 = .889,$$

$$p_2 = 49.0, \quad l_2 = 2.089,$$

so that  $l_2 - l_1 = 1.2$  foot ( $l_2$  corresponds to the part of the stroke at which the exhaust-valve opens), it is evident that

$$\int_{l_1}^{l_2} q \cdot dl = 169.5 + \int_{l_1}^{l_2} p \cdot dl. \quad \dots \quad (7)$$

Or if  $q_m$  is the mean value of  $q$  during this portion of the stroke, and if  $p_m$  is the mean value of  $p$ , then

$$1.2 q_m = 169.5 + 1.2 p_m,$$

or

$$q_m = 141.25 + p_m.$$

We find from the diagram that  $p_m = 94.5$ , so that  $q_m = 235.75$ .

Now  $1.2 A q_m$  is  $H$ , the total heat given to the fluid to alter its volume and pressure until the exhaust-valve opens;  $1.333 A \times 61.52$  is the indicated work  $W$  of the cycle, as calculated from the total indicator-diagram, including the dismission and suction parts not shown in fig. 1.

Hence  $H = \frac{1.2 \times 235.75}{1.333 \times 61.52} W$ , or  $3.45 W$ .

As we know that combustion, about the period of opening of the exhaust-valve, is just sufficient to supply the loss by radiation to the cylinder without having much effect on the volume and pressure of the fluid, we can assume that any combustion after that time produces heat which is radiated to the cylinder. We are told that there is no combustion in the exhaust. For the small amount of combustion after the exhaust-valve opens we do not see our way at present to the basis of any but the very roughest assumption, and we think that attention ought to be paid to this matter in future investigations. What complicates the question is the fact that the mass of the fluid which radiates heat to the cylinder rapidly gets less after the exhaust-valve opens. To obtain a first approximation, we may assume that the heat of combustion after the exhaust-valve opens is equal to the work done in the forward stroke after that time—that is, 0·14 W.

The heat retained by the fluid is  $141\cdot25 \times A \times 1\cdot2$ , or 1·94 W.

The gases in the exhaust-pipe close to the cylinder are known to have a temperature not much greater than  $400^{\circ}$  C. Hitherto it has been customary to calculate the amount of heat carried off by the gases through the exhaust-pipe from the heat-capacity multiplied by the difference of temperature from that of the atmosphere. It must be remembered, however, that the total heat of combustion of coal-gas contains the latent heat of the steam produced, and that the exhaust gases carry off this heat. Hence the amount of about 0·95 W, deducible from the experiments of Messrs. Brooks and Steward, must be increased by two thirds of itself, giving 1·57 W as the energy carried off by the gases in the exhaust-pipe.

Hence  $(1\cdot94 - 1\cdot57)$  W, or 0·37 W, is the amount of energy which is lost by the fluid from the opening of the exhaust-valve until the fluid is passing along the exhaust-pipe outside the cylinder. This is largely expended in heating the cylinder itself, in friction at bends in the exhaust-valve, &c. ; so that it disappears as radiated heat, and as heat given to the water-jacket during the remaining parts of the cycle. Now we may safely take it that the expenditure of gas is about 22 cubic feet per hour per indicated horse-power; so that, using the heat of combustion calculated in Table I., the total energy of combustion of the gas used is 5·91 W ; and we are now in a

position to make the following table. Of the 5.91 W, the total energy of combustion of a charge, we have:—

- 1.38 W. Work of forward working-stroke till exhaust-valve opens.
- 0.14 W. Work of forward working stroke after exhaust-valve opens.
- 2.31 W. Heat given to the cylinder during forward working stroke by radiation before exhaust-valve opens\*.
- 0.14 W. Heat of combustion after exhaust-valve opens and which is radiated to the cylinder.
- 1.57 W. Heat carried off by gases in exhaust-pipe.
- 0.37 W. Given to the cylinder as heat after the exhaust-valve opens, partly by friction at the exhaust-valve, partly during the succeeding three fourths or non-working parts of the cycle.

It is found by experiment that the water from the water-jacket carries off somewhat more than 50 per cent. of the total heat of combustion, or 2.96 W; but it is almost impossible to make this measurement accurately for one cycle. It is sometimes as much as 62 per cent. and sometimes as little as 35 per cent. We have not employed such a measurement here, partly for this reason, and partly on account of the rate of loss during three fourths of the cycle being indeterminate. Again, the cylinder loses heat by radiation as well as by the water-jacket; so that, even if we could assume that such a number as 50 per cent. is correct, we are still not in a position to state the total loss of heat from the cylinder.

\* It may be well to state here that we do not know with certainty the amount of gas used per indicated horse-power when the particular diagram which we are discussing was being taken, nor are we quite sure that Mr. Clerk is right in saying that the exhaust-gases show complete combustion when the engine is working to its full power. Our arrangements for determining this latter point are now nearly complete. We consider that there was no possibility of the expenditure having been less than 20 cubic feet per hour per indicated horse-power when our diagram was taken; and if we take 24 as a higher limit, and assume with Mr. Clerk that combustion is complete in the exhaust-pipe, we find the amount of heat given to the cylinder during the forward-working stroke by radiation before the exhaust-valve opens could not have been less than 1.77 W, the higher limit giving 2.85 W.

It is to be remembered that  $W$  is the indicated work. The useful work of a gas-engine, given out by the crank-shaft, is about  $0.8 W$ , there being an expenditure of  $0.2 W$  in overcoming the mechanical friction of the engine.

10. It is unnecessary to put before the Society the curves obtained by us by employing (6) on the discontinuous expressions of § 7 for the indicator-diagrams.

11. *Rate of Loss of Heat by the Fluid during Compression.*—For the compression part of the diagrams,

$$\gamma = 1.385,$$

and

$$p = 39.36 l^{1.304}.$$

Rate at which heat is received by fluid is  $-q$ , if

$$q = \frac{1}{\gamma-1} \left( \gamma p + l \frac{dp}{dl} \right);$$

and by § 8,

$$-q = \frac{36.36 l^{1.304} (m-\gamma)}{\gamma-1}$$

$$-q = l^{1.304} 39.36 \times \frac{m-\gamma}{\gamma-1},$$

$$m-\gamma = -0.081,$$

$$\gamma-1 = 1.385.$$

Therefore the rate at which heat is received by fluid is

$$-0.2104 p,$$

being proportional to the pressure, and is negative—that is, the fluid is radiating heat to the cylinder.

12. *Rate at which Fluid radiates Heat to cold Cylinder.*—It was found by the pyrometric measurements of Messrs. Brooks and Steward that the temperature of the products of combustion in the clearance-space, if there has been a recent explosion, is about  $410^\circ$  C.; and for the purpose of determining the temperature of the fluid before compression, they take 1.4 volume of coal-gas and 9.25 of air at  $22^\circ$  C. with 7.94 volumes of products of past combustions at  $410^\circ$  C., from which, assuming that the specific heats of the constituents do not alter with temperature, they find that the temperature of the mixture before compression is  $120^\circ$  C. This is sufficiently correct for our present purpose, and if we take it as the tempe-

rature when  $l = 2.222$ ,  $p_0 = 14.7$ , we can find the temperature corresponding with any point of any of the indicator-diagrams. We have made the calculations for various points on curve A B C D (fig. 1), knowing that  $pl \div T$  is constant (see § 3).

TABLE VIII.

$l$ .	$p$ .	Absolute temperature. T.	Tempera-ture of fluid. $t$ ° C.	$t$ ° - 60° C.	Ordinate of semicircle.	Ratio.
.889	44.5	476	203	143	0	$\infty$
.949	86	982	709	649	28	23.18
.989	105	1244	974	914	35.5	25.74
1.089	126	1644	1371	1311	48	27.33
1.389	90	1496	1223	1163	65	17.89
1.689	66	1344	1071	1011	66	15.32
2.089	49	1231	958	898	40	22.45

From some diagrams examined by us we find that the fluid may have as high a temperature as 1900° C.

The temperature of the water leaving the water-jacket was about 60° C. ; and we may for our purposes assume that the rate at which the fluid loses heat to the cylinder is proportional to the excess of its temperature above 60° C., so that  $t - 60$  represents, to some scale, the fluid's loss of heat to the cylinder per second. This rate of loss is shown on the curve A B (fig. 6).

Now if  $H$  is the quantity of heat which has been given by the fluid to the cylinder-jacket at the time  $\tau$ , then  $\frac{dH}{d\tau}$  is represented by the ordinate of the curve A B. But

$$\frac{dH}{d\lambda} = \frac{dH}{d\tau} \frac{d\tau}{d\lambda} \text{ or } \frac{dH}{d\tau} \div \frac{d\lambda}{d\tau};$$

and as the piston-motion is very nearly

$$\lambda = r(1 - \cos a\tau),$$

$$\frac{d\lambda}{d\tau} = ra \sin a\tau;$$

that is,  $\frac{d\lambda}{d\tau}$  is proportional to the ordinate of a semicircle C E F.

Describing the semicircle C E F with a diameter equal to the

length of the stroke, and dividing the ordinates of A B by those of C E F, we obtain the curve G H I, whose ordinate at any point represents the rate of the fluid's loss of heat to the cylinder per foot of piston-motion ; so that the whole area C G H I F represents the total loss of heat to the cold cylinder during the stroke. We are in a position to speak of the loss of heat from  $\lambda=0$  to  $\lambda=1.2$  (see § 9).

This loss must be represented on the diagram to the same scale as the indicator-diagram represents work done, and it is expended in the part of the working stroke from  $\lambda=0$  to  $\lambda=1.2$ . Hence if  $k$  is the mean ordinate of such a diagram,

$$k = 2.31 \times 61.52 \times 1.330 \div 1.2 = 158.$$

Now the mean ordinate of the curve G H I (fig. 6) from  $\lambda=0$  to  $\lambda=1.2$  being taken and found different from 158, all the ordinates of G H I (fig. 6) have been diminished in the proportion of 158 to the mean ordinate of G H I (fig. 6) to get the diagram X L Y of fig. 4. This diagram X L Y represents the rate of loss of heat by conduction and convection from the fluid to the cylinder during the working stroke until the exhaust-valve opens.

13. *Rate at which Combustion goes on during the Stroke.*—The curve E F G H represents the rate at which heat is actually gained by the fluid, and X L Y shows the rate at which heat is wasted to the cylinder ; so that the curve I J K Y shows at every point the rate at which heat is being generated in the fluid by combustion. It is obvious, then, that combustion is not complete at the end of the explosion part of the curve, although, as Mr. Clerk's experiments prove, the mixture of air and gas is in the proper proportions for explosion immediately behind the piston at all periods of the compression-stroke. The diagram I J K Y is specially valuable, as showing the effect of dissociation of the products of combustion at such temperatures as obtain in the gas-engine, and are shown in Table VIII.

*POSTSCRIPT, added June 10th.*—We have assumed in the paper that the rate of loss of heat by radiation and convection is proportional to the difference between the mean temperature of the fluid and the temperature of the cylinder. When we have more information concerning the distribution of heat in

the fluid, and the way in which a heated fluid loses its heat to a cold enclosing vessel, a more accurate assumption may be made; and it is easy to see what alteration this will introduce in our method of obtaining the curve  $XLY$  (fig. 4).

It is known from the experiments of MM. Dulong and Petit that the rate of cooling by radiation and convection of a solid body increases more rapidly than the difference of temperature, and that it is greater at greater pressures of the gaseous medium between the hot body and the surrounding cold vessel.

We are now engaged in an investigation involving much higher differences of temperature than those of MM. Dulong and Petit; and in so far as we have obtained results for temperatures extending from about  $800^{\circ}$  C. to  $1300^{\circ}$  C., we have confirmed the conclusions of these gentlemen. Thus the loss of heat per second at  $776^{\circ}$  C. being  $97.2$ , the loss at  $1292^{\circ}$  C. is  $253.2$ .

Our method of experimenting is, we believe, new. The heated body is a spiral of platinum, whose change of electric resistance when there is change of temperature is known. It is surrounded by a vessel, blackened inside and maintained at constant temperature. An electric current is made to pass through the platinum spiral, maintaining it at any required temperature. An ammeter and voltmeter enable the current  $A$  and the difference of potentials  $V$  between the ends of the platinum spiral to be measured. Then  $VA$  is the rate at which heat is being radiated from the platinum, and  $V/A$  is the electric resistance of the platinum, from which its temperature is known. We intend to investigate the influence of high pressures of air and other gases.

We are somewhat doubtful as to the weight which we ought to give to the results obtainable from these experiments on the loss of heat by solid bodies, since in our gas-engine investigations we deal with a mixture of hot gases; and in adopting the law of simple proportionality to difference of temperature, we have been influenced by the fact that rate of loss of heat by the fluid in the compression-stroke increases much more slowly than is indicated in Dulong and Petit's law, although the pressure of the fluid is increasing as well as its temperature. The result given in § 11 is to the effect that during compression the rate of loss of heat by the fluid is

nearly proportional to the  $\frac{1}{2}\frac{2}{3}$  power of the absolute temperature of the fluid, or to

$$(\theta + 333)^{\frac{1}{2}\frac{2}{3}},$$

if  $\theta$  is the difference of temperature from  $60^{\circ}$  C., the temperature taken as that of the cold cylinder. If  $q$  is this rate of loss, it is obvious that  $\frac{dq}{d\theta}$  diminishes as  $\theta$  increases. It will be observed that the probability of the piston's having a high temperature causes this result to be even more curious than it might otherwise appear to be.